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Evaluation of Waste Corn Cob and Copper Slag for Production of Novel Leakage-free Composite Phase Change Material with Improved Thermal Energy Storage

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Abstract

In this study, a leakage-free and thermally stable composite phase change material (PCM) was developed using waste corn cob (CC) and waste copper slag (CS) to evaluate renewable and waste biomass resources. MP-MS eutectic mixture was impregnated into a corn cob-derived carbon structure, and then, by adding CS at different ratios (1%, 3%, and 5%), the thermal performance was optimized. DSC analyses revealed that the melting temperature and melting enthalpy of the CC/MP-MS (35%) composite PCM were 22.9°C and 81.4 J/g, respectively. Small changes were observed in these values with the addition of CS, but only a 1–2% decrease in enthalpy was observed. Furthermore, after 650 cycles of thermal cycling testing, only a limited decrease in the thermal performance of the composite PCMs was observed, demonstrating high thermal stability and cyclic durability. Thermal conductivity values increased significantly with the addition of CS. While the MP-MS eutectic mixture had a limited thermal conductivity of only 0.17 W/mK, this value reached 0.42 W/mK with the addition of 5% CS. IR thermal camera images demonstrate that increasing the CS content accelerates heat transfer and improves temperature distribution. Specifically, after a 25-

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minute heating period, the surface temperature of the composite PCM containing 5% CS was approximately 9 °C higher than that of the pure composite.

Keywords: Waste Corn Cob; Copper Slag; Thermal Energy Storage; Phase Change Material; Energy and Energy Efficiency

Nomenclature

Nomenclature	
CC	Corn Cob
MP	Methyl Palmitate
MS	Methyl Stearate
MP-MS	Eutectic mixture of MP and MS
CS	Copper slag
PCMs	Phase Change Materials
LHS	Latent heat storage
LHTES	Latent heat thermal energy storage
TES	Thermal energy storage
SSCPCM	Shape-stable composite phase change materials

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Introduction

Phase change materials (PCMs) play a critical role in thermal energy storage (TES). Due to their high latent heat storage capacity, they absorb or release a large amount of energy during phase transition (solid-liquid). This feature enables passive regulation of indoor temperature fluctuations in building applications, thereby reducing heating/cooling energy consumption and carbon emissions. Form-stable composites such as fatty acid/wood flour composite PCMs (102.6 J/g latent heat) [1] or alkali-activated biochar-supported stearic-palmitic acid (127.69 J/g) offer long-term thermal reliability (>600 cycles) by preventing leakage [2]. Lab-scale tests have confirmed that building elements equipped with these materials reduce the internal temperature difference by 2–4°C [3]. The use of renewable support matrices (wood fiber, biochar) makes PCMs effective TES solutions in building envelopes with the advantages of low cost and environmental sustainability.

The widespread use of PCMs in energy storage systems is quite attractive, especially due to their high latent heat capacity. However, one of the main problems encountered by these materials in applications is the problem of leaching during the solid-liquid phase transition

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fact that PCMs turn into a liquid state when their melting point is exceeded limits their use, especially in fixed geometry systems such as building materials[4,5]. In order to prevent this problem, shape-stable composite phase change materials (SSCPCM) have been developed. In these systems, PCMs are adsorbed into porous carrier materials to provide structural stability and prevent leaching [4,6]. Among the porous support materials developed for this purpose, expanded graphite [7], diatomite [8,9], silica aerogel [10], vermiculite [11], silica matrices [12], activated carbon [13] and various biomass-based materials attract attention 4-6. In contrast to conventional inorganic adsorption materials, biomass-based porous support materials (such as moss [14], pomelo peel [15], radish [16], and wood [17,18] have garnered significant interest due to their ecologically benign, renewable nature, and high loading capacity.

Another major limitation of organic phase change materials (PCMs) in thermal energy storage applications is their inherently low thermal conductivity, which hinders efficient heat transfer during the melting and solidification processes. This drawback often leads to delayed charging and discharging rates, reducing the overall performance of PCM-integrated systems [19,20]. For instance, delignified wood-based composites were reported to maintain internal temperatures for longer durations due to their low thermal conductivity, making them suitable for insulation but less effective for applications requiring rapid thermal response [19]. Similarly, biomass-derived composites such as corn cob- and garlic peel-supported PCMs exhibited improved thermal energy storage behavior, but still suffered from low heat transfer rates, necessitating modifications or additives to enhance conductivity [5,21]. To address this issue, researchers explored the incorporation of thermally conductive additives such as expanded graphite, carbon fibers, or metal nanoparticles to significantly improve the heat transfer properties of composite PCMs, while balancing shape stability and latent heat capacity [21,22].

In order to overcome the leaching problem of phase change materials (PCM) and increase their thermal conductivity, the use of biomass-based carbon materials such as agricultural and forest wastes as supporting matrices is becoming increasingly widespread. Materials such as rice husk ash, coconut shell, pine cone biochar and carbonized wood fibers are low-cost and renewable, and increase the thermal energy storage capacity of PCMs by maintaining their shape stability [23-26]. Especially, biochar, due to its porous structure and high surface area, prevents PCMs from flowing during the transition to the liquid phase and increases heat conduction [27,28]. For example, Wen et al. [29] reported that the cycle stability was high and the thermal conductivity increased tenfold in PCM composites prepared using carbonized cellulose [29]. Similarly, palmitic-lauric acid-based composites prepared with rice husk charcoal solved the leaching and low thermal conductivity problems [30]. In biochar-supported

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dodecanoic acid-based systems, leakage was successfully prevented by capillary action, surface functionality and pore restriction mechanisms. In such studies, it was stated that the PCM:biochar loading ratio of 3:1 provided optimum performance [31]. In addition, it was observed that carbon-supported composite PCMs derived from biomass sources such as sugar cane pulp, water hyacinth and yellow oleander also gave successful results [32].

Composite PCMs prepared with materials such as activated carbon, carbonized apricot kernel shell and carbonized corn stalk provided significant increases in both thermal conductivity and energy storage density [29,33]. For example, the thermal conductivity in PA-LA (palmitic-lauric acid) composite supported by carbonized abandoned rice increased approximately 1.83 times compared to pure PCM [33]. Thermal conductivity also increased by 189% in composite PCMs prepared with a mixture of carbonized lotus shell and n-docosane [34]. Using PEG/GO/sisal fiber cellulose composites, Jia et al. [35] raised the thermal conductivity to 0.54 W/mK, and the dynamic impregnation process produced a uniform distribution. By speeding up heat transmission, GO's large surface area enhanced energy storage performance [35].

In various studies conducted to eliminate the leakage problem, biomass-derived carbon materials have been studied as effective support structures. To address this deficiency, mineral-based form stabilization and encapsulation strategies (e.g., encapsulation of PCMs using diatomite, silica, and other inorganic matrices), which have been widely investigated in recent years, have been reported in the literature to have made significant progress and to provide high thermal stability and improved leakage resistance [36-38]. The carbonized form of corn cob (CNCC) allowed lauric-stearic acid-based PCMs to be kept 77.9% leakage-free and thanks to the high porosity of these structures, both an increase in thermal conductivity by 87.5% and shape stability were achieved [39]. Activated carbon (AC) obtained from corn cob significantly reduced leakage by physically adhering palmitic acid (PA) to the porous structure. In this study, the high surface area (1364.7 m^2/g) and mesoporous structure of AC supported the fixation of PA in the structure. In addition, high thermal stability and leakage-free energy storage performance were observed after 10 cycles [40]. Similarly, in the PA/PB composite prepared with biochar (PB) produced from pine cones, palmitic acid was physically held by the support structure and this structure prevented leakage. This composite has also been improved in terms of thermal stability and conductivity (thermal conductivity increased by 43.76%) [26]. In activated carbon (AGP) based composites obtained from garlic peel, shape stability was achieved by successfully impregnating paraffin into the porous structure, and only 1.5% latent heat loss was observed at the end of 200 cycles [5]. In addition, it was determined that thermochromic PCMs impregnated with vacuum systems containing

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delignified wood were kept leak-free, and in addition, they provided thermal insulation and visual phase change advantages [19]. Biomass-based carbon materials (biochar, activated carbon, carbonized structures, etc.) enable the physical support of phase change materials and significantly reduce the leakage problem thanks to their high surface areas, porous morphologies and chemical stability. This allows PCMs to be used effectively and with long life in buildings and solar energy storage systems.

Traditionally, activated carbons obtained by carbonizing biomass at high temperatures have been used as support materials for the impregnation of PCMs. However, this method has disadvantages such as high energy consumption, long process time, need for chemical activation and therefore high-cost [41]. In recent years, in order to simplify this process and reduce environmental impacts, studies on directly impregnating biomass with PCMs without subjecting it to carbonization have increased. Thanks to this approach, energy and time are saved by eliminating the carbonization step, the process is simplified and the workload is significantly reduced. At the same time, the direct conversion of agricultural wastes into a high value-added energy storage material provides an environmental benefit in terms of waste management and offers an alternative compatible with sustainability goals [42,43]. For example, Chen et al. [6] produced a form-stable PCM composite by directly impregnating almond shells with PEG and reported that this method offers high thermal stability and low leakage properties. Similarly, it has been reported that high energy storage capacity, lightweight and cyclically stable composites can be produced because of the direct combination of aerogels obtained from orange peel biomass with PCM [44]. Hekimoğlu et al. [45] obtained high latent heat capacity and resistance to leakage by impregnating a natural support material based on walnut shell with methyl palmitate (MP). In addition, it has been stated that other agricultural wastes such as coffee grounds can be directly impregnated with PEG without carbonization and effective thermal energy storage composites can be produced [46]. In line with these studies, direct impregnation methods that do not require carbonization offer significant advantages in terms of both environmental sustainability and cost effectiveness and are considered a promising strategy for biobased energy storage systems in the future.

In this study, there are several important reasons for choosing the eutectic mixture of MP and methyl stearate (MS) as the organic phase change material (PCM). First, both components consist of saturated fatty acid methyl esters and are distinguished by their biodegradable and environmentally friendly properties. Combining methyl palmitate and MS in eutectic ratios provides a lower and more controlled melting point compared to their pure forms, providing an ideal phase transition temperature for certain applications. Furthermore, this eutectic

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mixture possesses high latent heat values, allowing it to store a high amount of thermal energy per unit mass. Other advantages of this eutectic system include low supercooling tendency, chemical stability, low evaporation loss, and non-toxicity [47-49]. Considering all these properties, the MP/MS eutectic mixture stands out as an organic PCM suitable for passive heat management in buildings, ensuring thermal comfort and for use in heat storage systems integrated with renewable energy.

Corn cob (CC) is an agricultural waste at huge quantities after leaving the corn parts. It is frequently used as bio-sorbent for cleaning organic and inorganic pollutants from wastewaters [50,51] as well as in the production of animal health products [52], agro-chemicals, veterinary formulations, vitamin premixes, pharmaceuticals [53] and building materials [54], etc. Besides, CC is in abundance in many regions of Turkey and national production can reach 3 x 10^6 ton per year [55]. The transforming of the CC to the value-added products is significantly rises its industrial and economic value. Additionally, the conversion of the CC from waste to product would expressively contribute to the reduction of environmental pollution in the world. Copper slag (CS) is a byproduct obtained through the copper extraction process by smelting. Before smelting process, the mechanically concentrated CS ores comprise mostly iron oxides and silicon oxides. The production quantity of CS diverges from 2.2 to 3 tons during the 1 ton-production of copper metal [56]. The projected annual CS production of is approximately 68.7 million tons, which creates an important environmental challenge when dumped in landfills instead of conversing to a valued resource [57] CS can be evaluated in the production of concrete by partially replacing with sand and used to form building material [58]. It can be proper for creating radiation shielding-buildings like healthcare centers [59]. Based on the evaluation awareness of CC and CS as cost-effective waste materials, this work is aimed to evaluate CC as carrier material for form-stabilization of eutectic mixture of MP and MS as an organic phase change material (PCM) to prevent its flow in molten case through the heating process. Therefore, for first time in this study, leakage-free CC/MP-MS(35 wt%) composite PCM was successfully produced for thermal regulative requests as well as notably boosted its thermal conductivity property by doped with CS powder as low-cost material.

Experimental

Materials

Methyl palmitate ($CH_3(CH_2)_{14}CO_2CH_3$, m.p: 32-35 °C; purity: ≥97%; density 0.852 g/mL at 20 °C) and methyl stearate ($CH_3(CH_2)_{16}CO_2CH_3$, m.p: 37-41 °C; purity: ≥96%; density 0.849 g/mL at 20 °C) was provided from Merck Company was used as a PCM. Copper slag (CS)

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was bought from Eti Gümüş Inc. Copper Enterprise (Elazığ, Türkiye). The average grain size of CS is shown in Figure 1 and the SEM image is shown in Figure 2.

Fig. 1. Grain size distribution of the Copper Slag (CS) sample.

The particle size distribution graph in Figure 1 shows that the Copper Slag (CS) sample has a multimodal particle system distributed over a wide size range. Analysis of the cumulative volume curve reveals that the average particle size, corresponding to 60% of the cumulative volume, is approximately 0-2 μm, while the remaining 90% is comprised of particles smaller than approximately 76 μm. This distribution indicates that the CS sample contains both fine and coarse particles and has a heterogeneous structure. Thanks to their small size, CC particles penetrate the micro/mesopores more easily, increasing capillary impregnation efficiency and providing a more homogeneous distribution on the pore walls when combined with PCM. Conversely, it is thought that larger particles may be located at the pore entrances or in larger voids, creating a partial bridging/blocking effect. While this may limit PCM penetration in some areas, it is also thought to contribute to thermal conductivity by increasing conductive phase contacts in macro voids.

Fig. 2. SEM images, EDS analyses and elemental composition (% by weight) of CS.

Copper slag (CS) has a complex structure containing primarily oxygen, as well as metallic and semimetallic elements such as Fe, Al, and Si. EDS maps reveal an irregular but broad distribution of these elements, while SEM images reveal tightly packed particles of varying sizes.

Preparation of the leakage-free composite PCMs

Firstly, MP-MS eutectic mixture was prepared with weight ratio of 87% MS and 13% MP as described in the literature [61]. The leakage-free CC/MP-MS/CS composite PCMs were produced via direct impregnation as cost-effective simple method. Here, CC was acted as carrier matrix for form-stabilization of the eutectic mixture against leakage problem while heating over its melting temperature. The flow diagram of the experimental method monitored for the manufacturing of this composite PCMs is demonstrated in **Fig. 3**. As noticeably understood from this schema, the CS in powder form was added to the MP-MS eutectic mixture in melted state and homogenised at 40 °C for 1 hours the CC powder was added to the pre-composite in sol-gel form and then homogenised again at 40 °C for 2 h. The final composite was poured in a plastic mould and cooled to 20 °C. The preparation process of composite was repeated by changing the weight fraction of MP-MS eutectic mixture as 25, 30, 35 and 40% while the weight amount of CS was varied as 1.0, 3.0 ad 5.0%. Afterwards, to control the form stability of the composite PCMs, each of composite samples was placed

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on the filter paper and heated up to 45 °C for 30 min using heating plate. Significant leakage was seen during the solid-liquid phase transition at 40% PCM content (visual inspection and filter paper method), suggesting that the CC/CS composite system's maximal impregnation capacity without leakage is 35%. The sample with no molten PCM leakage observed at the bottom was defined as leakage-free composite PCM. The photographs of leakage-free and non-leakage free composite PCMs were presented in Fig. 4(a). As clearly seen from these images, the maximum weight fraction of eutectic PCM in the composite was found as 35% and finally the produced CC/MP-MS(35%)/CS(1%), CC/MP-MS(35%)/CS(3%) and CC/MP-MS(35%)/CS(5%) was characterized as leakage-free composite PCMs. Moreover, the leakage ratios of MP-MS belonging to the prepared composite samples were determined at different heat treatment times, 10, 20 and 30 min and the results are presented graphically in Fig. 4(b). The increase in the amount of PCM (MP-MS) in the matrix structure (CC/CS) led to a significant leakage ratio due to the supporting structure reaching its saturation limit. For example, the leakage ratio of the composite containing 40% MP-MS was higher compared to the sample containing 30% and 35% MP-MS due to leakage during the examined heating periods. For the leakage-free composite PCM at 30th min, CC/MP-MS(35%)/CS(5%), the MP-MS leakage ratio was limited by only 1.45% while it was determined as 3.10% for the composite, CC/MP-MS(35%)/CS(5%).

Fig. 3. Experimental flow diagram monitored through the production of leakage-free CC/MP-MS/CS and CC/MP-MS/CS composite PCMs.

Fig. 4. (a) The photographs obtained after the leakage test of CC/MP-MS/CS composite PCM **(b)** MP-MS leakage ratio (%) of the composite samples after different heating periods at 45°C

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Characterization

The surface morphologies of CC, CC/MP-MS(35%) and CC/MP-MS(35%)/CS(5%) composite PCMs were realized by SEM analysis (ZEISS EVO LS 100 model). The EDS spectrum was also obtained to expose elemental composition of the CC/MP-MS(35 wt%)/CS(5%) composite. The chemical structures of CC, MP-MS eutectic PCM, CC/MP-MS and CC/MP-MS/CS(5%) composite PCMs were characterized using FTIR spectrometer (Shimadzu IRSpirit, QATR-S) at wavenumber range of 400-4000 cm^{-1}. The crystal structures of CC, CS, eutectic PCM and the composite PCMs was identified by XRD technique (PANalytical X0-Pert3 model) with Cu K radiation at wavelength of 0.154 nm and 2θ range of 5-90°. The LHTES characteristics of the produced eutectic PCM and composite PCMs was obtained by DSC analysis (HITACHI 7020 model) at the same heating/cooling rate as

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3°C/min under nitrogen gas flow. Each analysis was replicated three times and the mean deviation for melting/freezing temperature and enthalpy results were found as ±0.13°C and ±0.36 J/g, respectively. Thermal degradation steps of CC, eutectic PCM and composite PCMs were determined by using a TGA instrument (Perkin-Elmer TGA7, USA). The measurements were carried out at 10°C/min heating rate, 30-800°C and under argon gas flow.

The produced composite PCM samples were tested using a cycling device (^{3}Prime, Techne model) by following heating/cooling stages replicated 650 times between 15 °C and 40 °C. Thermal conductivities of MP-MS eutectic PCM, CC/MP-MS, CC/MP-MS/CS(1%), CC/MP-MS/CS(3%) and CC/MP-MS/CS(5%) composites were measured by a thermal analyzer (KD2-Pro Decagon). The measurements were repeated three times at 20 °C and the mean value with accuracy of ±5% was considered. The improvement in thermal conductivity was proved by determining the temperature dissemination into the composite samples during heating period samples using an infrared thermal camera (FLIR E5XT, accuracy: ±2%; heater bulb: 250 W).

Results and Discussion

Morphology and chemical structure analysis results

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Fig. 5. SEM photographs of (a) CC, (b) CC/MP-MS(35%) composite PCM, (c) CC/MP-MS(35%)/CS(5%) composite PCM.

The surface morphology of CC fibers exhibits a highly porous and irregular structure. This structure is characterized by pronounced grooves, cracks and voids, which provide the material with a unique high surface area. This natural porosity acts as an ideal "skeleton" for the efficient adhesion and absorption of other components, especially molten methyl palmitate-methyl stearate (MP-MS) mixture or CS particles, in subsequent modifications. It shows that 35% of MP-MS eutectic mixture was successfully impregnated into the CC skeleton. As a result of this process, it is observed that the original porous structure of CC is largely filled or covered. The surface acquires a smoother, less porous and more compact morphology. This morphological change confirms that the molten MP-MS mixture has effectively penetrated and absorbed into the macro and micro pores of CC. This successful impregnation is critical to prevent melt leakage during phase change cycles. It reveals that in addition to the CC skeleton impregnated with 35% MP-MS eutectic mixture, 5% CS particles were added by mass. The most prominent feature of this composite is the presence of small CS particles dispersed on the surface. These particles are either adhered to the surface or settled in the existing pores. The EDS analysis also shows the presence of 0.44% copper in

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the samples in **Fig. 5d**. While the characteristic features of the basic CC/MP-MS structure (surface smoothness and compactness) are preserved, the integration of CS particles into the surface is observed. The addition of these particles carries the potential for an increase in thermal conductivity due to the copper content. The internal fiber composition and structural arrangement of corn cob (CC) are critical factors that directly affect the overall mechanical properties of the material. CC, which is mainly composed of cellulose and lignin, exhibits remarkably high mechanical strength due to the synergy of these components. Structurally, the microstructure and associated mechanical properties of CC show a profile like that of wood, while its strength and overall mechanical performance are reminiscent of cork[60]. This unique composition and structural arrangement make corn cob potential material for various applications[21].

Fig. 6. FTIR spectra of CC, MP-MS eutectic PCM, CC/MP-MS and CC/MP-MS/CS (5%) composite PCMs.

The chemical structures and interactions of CC (corn cob), MP-MS eutectic PCM, and composite PCMs (CC/MP-MS and CC/MP-MS/CS (5%)) were assessed using FTIR studies (Fig. 6). The stretching vibrations of cellulose and hemicellulose-derived –OH groups are represented by the broad band in the range of 3150–3480 cm^{-1} in the CC spectrum, whereas aliphatic C–H vibrations are represented by the peaks in the range of 2845–2990 cm^{-1}. Furthermore, the lignocellulosic structure is confirmed by the signal at 1045 cm^{-1}, which is associated with C–O–C and C–O bonds. The C–H stretching vibrations of long-chain methyl esters in the MP-MS eutectic mixture are represented by the substantial peaks at 2918 and 2850 cm^{-1}, the carbonyl (C=O) group by the strong peak at 1741 cm^{-1}, and the ester C–O–C vibrations by the peak at 1168 cm^{-1}. PCM was physically impregnated into the porous structure without undergoing a chemical reaction, as evidenced by the composite spectra's preservation of distinctive peaks from both CC and MP-MS. A broadening and low-wavenumber shift was seen with the addition of CS, especially in the –OH band in the region of 3135–3550 cm^{-1}, which is linked to hydrogen bonding between the biomass structure and metal oxide/hydroxide groups. The lack of a shift or new peak creation in the C=O and C–O bands, however, indicates that there was no chemical reaction between CS and MP-MS and that the interaction was mostly physical. These findings show that the MP-MS eutectic mixture is successfully incorporated into the CC matrix while preserving structural integrity and are in line with comparable composite systems documented in the literature [61,62].

Fig. 7. XRD diffraction patterns of CC, CS, MP-MS eutectic PCM, CC/MP-MS and CC/MP-MS/CS(5%) composite PCMs.

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Fig. 7 presents the X-ray diffraction (XRD) patterns of Corn Cob (CC), Copper Slag (CS), MP-MS eutectic phase change material, and composites prepared with these components. The CC sample exhibited a semi-crystalline structure with two prominent diffraction peaks observed at 2θ = 15.33° and 21.44°. The eutectic mixture of MP and MS revealed the presence of ordered crystalline phases with six characteristic peaks located at 2θ = 7.25°, 10.95°, 14.66°, 20.92°, 22.99°, and 23.97°. The CS sample showed an inorganic multiphase structure with phases appearing at 2θ = 20.98°, 26.65°, 32.75°, 35.91°, 53.41°, and 58.85°. The presence of eutectic PCM in the CC/MP-MS composite was confirmed by the new phases observed at 2θ = 6.08°, 10.71°, 14.49°, 20.44°, 21.43°, and 23.85°, demonstrating the successful integration of MP-MS into the CC matrix and the establishment of crystalline interactions between the components. The CS-added composite (CC/MP-MS/CS(5%)) was characterized by peaks observed at 2θ = 6.98°, 11.07°, 13.96°, 20.39°, 21.65°, and 23.84°. These results indicate that the incorporation of CS into the structure causes slight shifts in the positions of the crystalline phases, and structural interactions occur. The constant number of crystalline phases and the small changes in the pixel positions indicate that the PCM was successfully fixed in the composite system and that the CS addition contributed to structural stability.

LHS properties of the leakage-free composite PCMs

DSC thermograms for the MP, MS and MP-MS Eutectic are displayed in **Fig. 8**. Additionally, LHTES data of these materials were tabulated in Table 1. Melting and freezing temperature of the pure MP, MS and MP-MS eutectic were measured as 31.8, 36.9, 24.4 and 26.4, 35.4, 23.4 °C and fusion and freezing latent heat of MP were found as 248.4, 234.6, 233.8 and -243.6, -238.7, -228.5 J/g, respectively. In their study, Hekimoğlu et al.[45] determined the melting temperature of pure MP as 28.13°C, freezing temperature as 25.44°C, melting enthalpy as 255.46J/g, and freezing enthalpy as -252.56J/g. Similarly, Abden et al.[63] developed phase change materials using MS and determined the melting temperature of pure MS as 38.94°C and melting enthalpy as 215.5J/g using DSC analysis. These values reveal that MS has a higher phase transition temperature compared to MP and offers a similar level of thermal energy storage capacity. In another study, the melting and freezing temperatures of pure MP were determined as 33.97°C and 23.92°C, and the melting enthalpy was 186.5J/g, respectively, and the melting and freezing temperatures of pure MS were determined as 41.89°C and 32.69°C, and the melting enthalpy was 179.1 J/g. The eutectic PCM obtained by mixing these two compounds in the MP:MS (90:10) ratio was measured as 27.24°C and the melting enthalpy as 164.1J/g [61].

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Fig. 8. DSC thermograms of pure MP, pure MS and MP-MS eutectic mixture.

Fig. 9 presents DSC thermograms of the heating-cooling cycles of CC/MP-MS eutectic composite phase change materials with different amounts of CS. In addition, melting and freezing temperatures and enthalpy values are given in Table 1 below. The pure CC/MP-MS(35%) composite showed a melting temperature of 22.9°C and a melting enthalpy of 81.4J/g; a freezing temperature of 22.6°C and a freezing enthalpy of 78.3J/g. In the sample containing 1% CS, the melting temperature decreased to 22.4°C and the melting enthalpy to 80.6J/g, while the freezing process also showed similar slight decreases (22.5°C, 77.1J/g). The composite containing 3% CS had a melting temperature of 23.3°C and an enthalpy of 79.1J/g. With the addition of 5% CS, the melting temperature reached its maximum value of 23.8°C, but the melting enthalpy decreased to 77.2J/g. These results indicate that the addition of CS resulted in a gradual increase in the melting temperatures of the composite PCMs, but a slight decrease in their enthalpy values. This suggests that CS has a limited effect on thermal energy storage capacity but can modulate the phase transition temperature upward. The metal oxides and inorganic phases present in CS enhance heat conduction within the composite structure, resulting in a more homogeneous distribution of thermal energy. This reduces localized overheating, potentially causing some components to decompose at higher temperatures and thus observing a shift in the decomposition temperature. Furthermore, the physical barrier effect created by the incorporation of CS limits the diffusion of volatile degradation products from the MP-MS phase change material and the biocarbon matrix. This can lead to a delay in thermal decomposition, especially at higher CS ratios. The reason why the addition of CS to PCM causes a partial increase in the phase transition temperature is explained by pore confinement and interface interactions between PCM and the porous matrix. A literature review explained, using Gibbs-Thomson theory, that strong surface interactions and confinement effects can alter the melting temperature depending on pore size and surface chemistry [64].

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Fig. 9. DSC thermograms of CC/MP-MS(35%), CC/MP-MS(35%), CC/MP-MS(35%)/CS(1%), CC/MP-MS(35%)/CS(3%) and CC/MP-MS(35%)/CS(5%) composite PCMs.

Table 1. The measured latent heat thermal energy storage (LHTES) properties of the produced leakage-free composite PCMs.

Table 2. Comparison of LHS capacities of the produced composite PCMs with those of various kinds of composite PCM.

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Table 2 presents the latent heat storage capacities of the composite phase change materials (PCMs) produced in this study in comparison with various biochar or inorganic-supported PCMs reported in literature. The comparison also includes the impregnation methods used. While vacuum impregnation is preferred for most samples reported in the literature, in this study, high-yield composites were obtained using the direct impregnation method. Data analysis reveals that the CC/MP-MS(35%) sample exhibits a high melting enthalpy of 80.6 J/g. Although the enthalpy value decreases to 79.1 J/g, and 77.2 J/g, respectively, as the CS addition ratio increases, these values are still higher than many composite PCMs reported in the literature. For example, when compared to palmitic acid/mullite (52.3 J/g), stearic acid/kaolin (66.3 J/g), or wood/paraffin wax (20.6 J/g) systems, the thermal energy storage capacity of CC/MP-MS-based composites is significantly superior. This can be explained by the high latent heat capacity of the eutectic MP-MS mixture used and the sufficient stabilization of the PCM by the CC matrix. Furthermore, although variations achieved with the addition of CS result in a slight decrease in enthalpy values, this addition is thought to be beneficial in terms of providing mechanical stability and potential functional properties to the structure. In conclusion, the composite PCMs developed in this study can be considered highly suitable and competitive alternatives for thermal management and energy efficiency applications in buildings thanks to their high latent heat storage capacities. Achieving high performance, particularly through direct impregnation without the need for complex processes such as vacuum, provides a significant advantage in terms of ease of application.

Pure PCMs are rarely used on their own in practical thermal energy storage systems because of important constraints like phase transition leakage and intrinsically low thermal conductivity. Therefore, even if it lowers the total latent heat capacity, the use of supporting matrices and additives is crucial. For many shape-stable composite PCMs described in the literature, particularly those based on biochar, porous minerals, or carbon compounds, the obtained value of about 80 J/g is still within the range. Additionally, the inclusion of CS greatly enhanced heat transfer efficiency—a critical characteristic for real-world applications—and thermal conductivity (up to 0.42 W/mK). By facilitating more effective charge/discharge cycles, faster heat transfer can make up for reduced energy density. Because it enables the creation of a leak-free, thermally stable, and more effective heat transfer material, the observed decrease in latent heat is therefore regarded as a reasonable and acceptable trade-off, making it more appropriate for real-world engineering applications like building thermal management systems.

Cycling LHS reliability and chemical stability of the leakage-free composite PCMs

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PCMs are frequently utilized in chronic situations. For PCMs, the stability of chemical structure and thermal performance is therefore crucial. The DSC curves of leakage-free composite PCMs before and after 650 cycles are shown in **Fig. 10**, and Table 3 provides a summary of the phase transition parameters. The DSC curves before and after 650 heat cycles almost overlap, indicating that leakage-free composite PCMs thermal performance is comparatively stable. Only limited changes were observed in both the melting and freezing temperatures and enthalpies of the composites after cycling. In the CC/MP-MS(35%) sample, the melting temperature increased slightly from 22.9°C to 23.0°C, while the melting enthalpy decreased from 81.4J/g to 80.2J/g. Similarly, the freezing temperature and enthalpy changed from 22.6°C to 22.7°C and from 78.3J/g to 77.3J/g, respectively. In the CC/MP-MS(35%) sample, the melting temperature decreased by 0.1°C, while the melting enthalpy decreased by 1.5%; the freezing temperature and enthalpy decreased by 0.1°C and 1.3%, respectively. This indicates that the PCM structure remains stable under thermal cycling. A similar trend was observed in the CS-added composites. For the CC/MP-MS/CS(1%) composite, the melting enthalpy decreased from 80.6J/g to 79.2J/g, while when the CS ratio was increased to 5%, the melting enthalpy decreased from 77.2J/g to 76.4J/g. Enthalpy losses for all composites remained between 1.2% and 2.5% after 650 cycles. No change was observed in the melting and freezing temperatures of the composite containing 1% CS; only the melting enthalpy and freezing enthalpy decreased by 1.7% and 1.0%, respectively. In the sample containing 3% CS, both the melting and freezing temperatures decreased by 0.1°C, while enthalpy losses of 1.4% and 1.2% were recorded, respectively. In the composite prepared with 5% CS, the melting temperature decreased by 0.1°C, but the enthalpy decreased by 1.0%. The freezing temperature increased by 0.1°C, while the freezing enthalpy decreased by 1.6%.

Fig. 10. DSC results of CC/MP-MS(35%), CC/MP-MS(35%)/CS(1%), CC/MP-MS(35%)/CS(3%) and CC/MP-MS(35%)/CS(5%) composite PCMs after first cycle and 650th cycle.

Table 3. LHTES properties of the leakage-free composite PCMs along with thermal cycling number.

Within this study, the reliability and chemical stability of PCMs were evaluated using repeated thermal cycling [72]. As illustrated in **Fig. 11**, the FTIR spectra prior to and following thermal cycling are contrasted. The location and form of the absorption peaks in the FTIR spectra have not changed noticeably after 650 heat cycles, suggesting that the chemical structure of the composite has not changed because of repeated melting and freezing

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procedures. These ratios demonstrate that PCMs can maintain their high thermal cycling resistance and phase transition performance for extended periods. Consequently, the leakage-free composite PCMs exhibit excellent structural and chemical stability.

Fig. 11. FTIR spectra of CC/MP-MS(35%) and CC/MP-MS(35%)/CS(5%) composite PCMs at first cycle and 650th cycle.

Thermal degradation stability of the produced leakage-free composite PCMs

Fig. 12 shows the TGA curves, exhibiting the thermal stability of pure MS-MP eutectic PCM, pure CC, CC/MP-MS(35%) and CC/MP-MS(35%)/CS(5%) composite PCMs. Pure MS-MP eutectic PCM displays one-step degradation shape, with an initial 2% weight loss below 178 °C related with the evaporation of volatile residues. A significant mass loss of 97.2% between 178 °C and 334 °C corresponds to the decomposition of volatile degradation products. Pure CC shows the degradation between 30 °C and 195 °C with mass loss of 2% due to evaporated water retained into cellular structure of the CC while its hemicellulose and cellulose ingredients are decomposed in the range of 195-392 °C corresponding to mass loss of 67.2%. The rest of the curve is attributed to the thermal decomposing of non-volatile stable phenolic lignin residues [73]. In contrast, the CC/MP-MS(35%) composite lost 2% of its total mass at interval of 30-182 °C as it lost mass of about 62% up to 335 °C. This means that thermal degradation of the impregnated MS-MP completely matched with thermal composition of hemicellulose and cellulose constituents of CC. Moreover, the same mass losses of the CC/MP-MS/CS(5%) composite occurred in temperature range of 30-212 °C and 212-340 °C. The somewhat shift in the decomposition could be owing to slightly enhanced thermal resistance by CS content of the composite. Furthermore, these results suggest that initial values of decomposition temperatures of both CC/MP-MS(35%) and CC/MP-MS(35%)/CS(5%) composite PCMs are greatly higher than the working temperature (~24 °C) of MP-MS eutectic PCM, revealing the outstanding suitability for their usage in TES practices.

Fig. 12. TGA curves of pure CC, pure MP-MS eutectic mixture, CC/MP-MS(35%) and CC/MP-MS(35%)/CS(5%) composite PCM.

Thermal conductivity improvement results of the leakage-free composite PCMs

The thermal conductivities of the pure MS-MP eutectic PCM, CC/MP-MS(35%) and CC/MP-MS(35%)/CS composite PCMs were analyzed and the results are presented in **Fig. 13**.

Fig. 13. Thermal conductivity values of MP-MS eutectic mixture, CC/MP-MS(35%), CC/MP-MS/CS(1%), CC/MP-MS/CS(3%) and CC/MP-MS/CS(5%) composite PCMs.

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According to the results presented in **Fig. 13**, the thermal conductivity of the MP-MS eutectic mixture was measured as 0.17 W/mK, a value typical for organic PCMs with low thermal conductivity. The thermal conductivity of the CC/MP-MS (35%) composite formed by MP-MS with corncob (CC) matrix increased to 0.22 W/mK. These values increased further with the addition of copper slag (CS); thermal conductivity values were determined as 0.28, 0.33, and 0.42 W/mK with 1%, 3%, and 5% CS additions, respectively. The increase in thermal conductivity as the CS ratio increases is striking, clearly demonstrating the thermal conductivity-enhancing effect of CS. In particular, the 5% CS addition achieved a thermal conductivity value approximately 2.5 times higher than the initial MP-MS eutectic PCM.

These findings support previous studies indicating that copper-based additives increase the thermal performance of composite PCMs. For example, Xiao et al.[74] reported that the thermal conductivity of the copper foam/paraffin composite PCM they prepared by vacuum impregnation method was approximately 15 times higher than that of pure paraffin. Similarly, Ye et al.[75] emphasized that metal-added PCMs exhibited high thermal conductivity along with high latent heat capacity, significantly increasing the heat storage density and heat exchange efficiency. Xiao et al.[76] determined the thermal conductivity of the copper foam/ hydrated salt of sodium acetate trihydrate (SAT) composite PCM they developed as 2.10 W/mK, and stated that this value was 1.76 times higher than that of pure SAT systems. Li et al.[77], it was reported that the thermal conductivity of copper foam-supported the SAT composite increased by 11 times compared to pure SAT, while the volumetric heat storage capacity was 2.2–2.5 times that of conventional water tanks.

Table 4 presents the thermal conductivity values of the composite PCMs developed in this study compared to paraffin-based PCM systems supported by different carbon materials in the literature. According to table 4, the total thermal conductivity of composite PCMs varies depending on both the thermal conductivity of the carrier material impregnated with the PCM and the thermal conductivity and ratio of the carbon-based material added as an additive. The CC/MP-MS(35%) sample developed in this study had a relatively low conductivity of 0.22 W/mK, but this value increased to 0.28, 0.33, and 0.42 W/mK with 1%, 3%, and 5% copper slag (CS) addition, respectively. In particular, the CC/MP-MS(35%)/CS(5%) composite exhibited higher thermal conductivity compared to many paraffin-carbon-based PCM systems reported in the literature. For example, Garlic Stem Biochar/paraffin composites offer thermal conductivities in the range of 0.28–0.31 W/mK[78], while Phoenix leaf biochar/stearic acid systems offer thermal conductivities in the range of 0.33–0.41 W/mK[79], while some CNT-supported systems have reached levels of 0.15-0.30 W/mK[80,81]. These

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results demonstrate that the thermal conductivity-enhancing effect of copper slag is comparable to that of commonly used activated carbon, CNT, or biochar additives. Furthermore, when combined with a low-cost and sustainable matrix such as CC, CS-supported composite PCMs appear to offer both environmentally and economically viable and efficient thermal energy storage materials.

Table 4. Comparison of thermal conductivity of the produced composite PCMs with those of different kind of paraffin based PCM/carbon material.

Fig. 14 presents infrared (IR) thermal camera images from a heating experiment conducted to verify the effect of CS (copper slag) on increasing the thermal conductivity of CC/MP-MS(35%) composite PCMs. These images comparatively reflect the temperature changes of composite samples with different CS ratios during the heating period. As can be clearly seen from the images, a significant increase in the temperature increase rate of the samples was observed as the CS ratio increased during the heating period. For example, at 10 minutes, the surface temperature of the CC/MP-MS(35%) sample was 32°C, while the values measured for samples containing 1%, 3%, and 5% CS were 32.9°C, 33.5°C, and 34.8°C, respectively. When the heating time was increased to 15 minutes, the temperature difference compared to the reference composite reached 1.4°C, 4.9°C, and 8.9°C, respectively. When the time was extended to 25 minutes, these differences increased further, reaching 3.8°C, 5.8°C, and 9.0°C, respectively. These findings clearly demonstrate that heat propagates more rapidly within the composite due to an increase in the CS doping ratio, resulting in higher surface temperatures. This is primarily due to the significant increase in thermal conductivity of the composite PCM with the incorporation of CS. This is confirmed by previous thermal conductivity measurements, particularly as the sample containing 5% CS exhibits the highest thermal conductivity (0.42 W/mK) and the fastest heating profile.

Fig. 14. IR thermal camera images of CC/MP-MS(35%), CC/MP-MS/CS(1%), CC/MP-MS/CS(3%) and CC/MP-MS/CS(5%) composite PCMs during heating period.

Conclusion

In this study, composite phase change materials (PCMs) were produced by impregnating a waste corncob (CC)-based carrier matrix with a eutectic mixture of methyl palmitate (MP) and methyl stearate (MS). Furthermore, the effect of waste copper slag (CS) on the thermal and physical properties of these composites was investigated in detail. The prepared CC/MP-MS and CS-doped variations exhibited leak-free structures, and form-stable composite PCMs were successfully obtained.

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Differential scanning calorimetry (DSC) analyses revealed that all composites had suitable melting/freezing temperatures (22–24 °C) and high latent heat storage capacities (77-81 J/g). Enthalpy losses of only 1-2% were observed after 650 thermal cycles, demonstrating the long-term thermal stability of the composites. Thermal conductivity measurements showed that while the pure MP-MS mixture was 0.17 W/mK, this value increased to 0.42 W/mK in the composite containing 5% CS. IR thermal camera data demonstrate that copper slag doping not only increases thermal conductivity values but also significantly improves the heat transfer efficiency of composite PCMs. This suggests that CS-doped PCMs are particularly strong candidates for thermal energy storage systems, where rapid thermal response is critical.

XRD analyses showed that CS maintained its crystalline structure, while MP-MS and CC largely retained their structural properties after eutectic mixing. Furthermore, the composite PCMs obtained in this study were found to outperform many carbon-based reinforced PCMs in literature in terms of thermal conductivity.

In conclusion, this study demonstrated that CS additive can be used not only as an environmentally friendly waste recycling agent but also as an additive to enhance thermal performance. The developed CC/MP-MS/CS composites have the potential to be used with high efficiency in applications such as passive thermal management and thermal energy storage systems, particularly in buildings. Corn cob, due to its organic structure, is susceptible to bacterial and fungal growth under humid conditions, is inherently flammable, and can lead to swelling, dimensional instability, and reduced mechanical integrity. Furthermore, the long-term mechanical durability of CC-based composites under repeated thermal cycling and environmental aging has not yet been proven. To overcome these challenges, future studies should investigate surface treatments (e.g., hydrophobic coatings or antifungal agents), flame-retardant additives, or encapsulation strategies. Until these issues are resolved, corn cob-based PCM composites are considered most suitable for non-load-bearing and low-humidity indoor applications.

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CRediT authorship contribution statement

Ahmet Sarı: Conceptualization; Writing – review & editing, Supervision. **Ahmet Can:** Supervision, Resources, Writing – original draft. **Yusuf Er:** Investigation, Methodology, **Vedat Veli Çay:** Investigation, Resources. **Osman Gencel:** Writing – original draft, Writing – review & editing. **Vineet V. Tyagi:** Writing – review & editing

Declaration of Competing Interest

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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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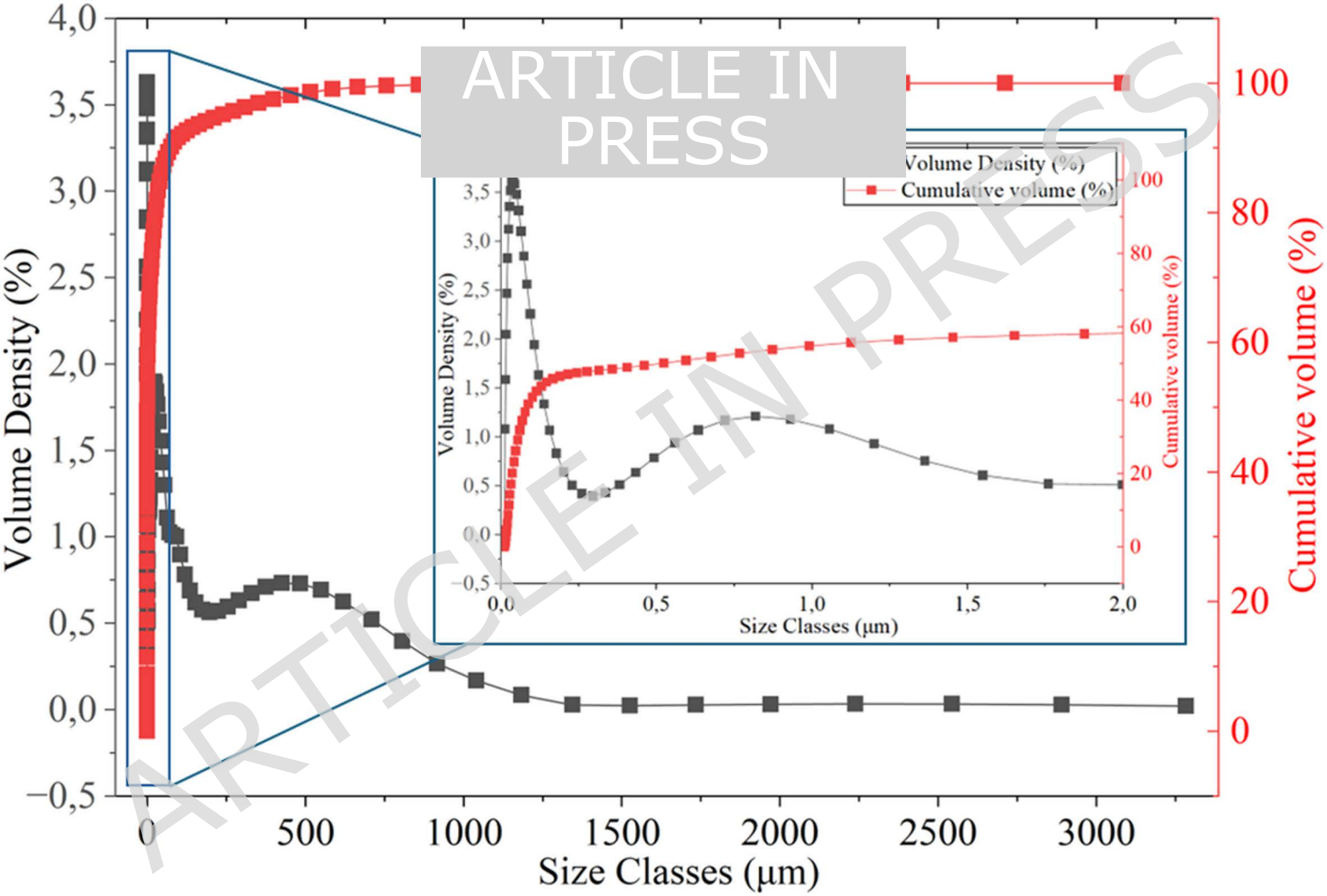

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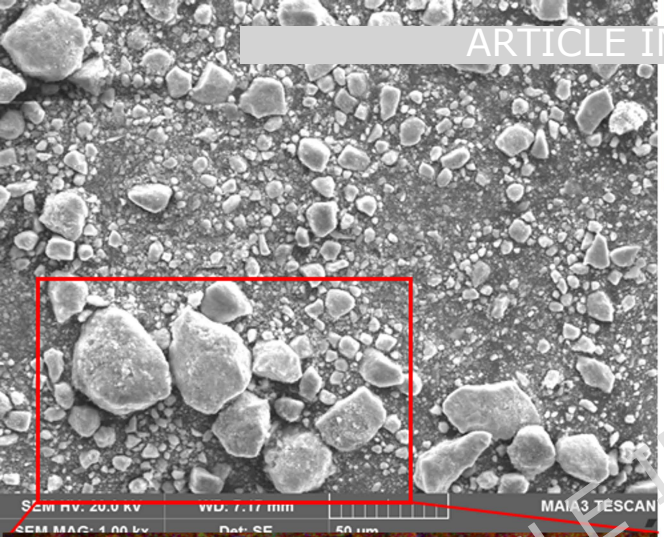



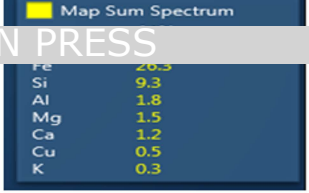

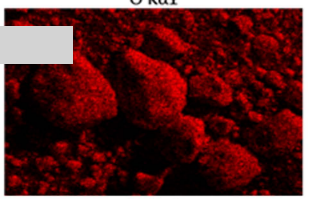



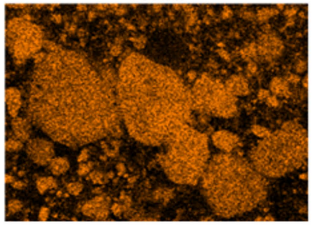

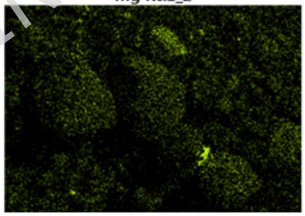

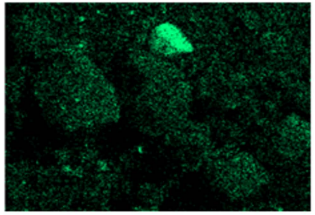

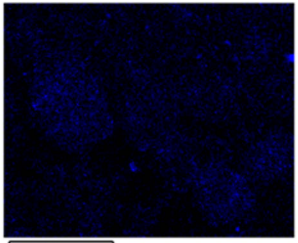

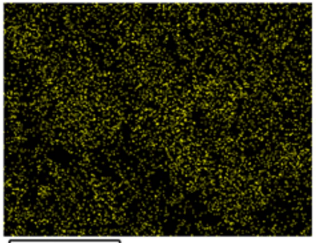

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Corn Cob (CC)



grinding process



CC in powder form

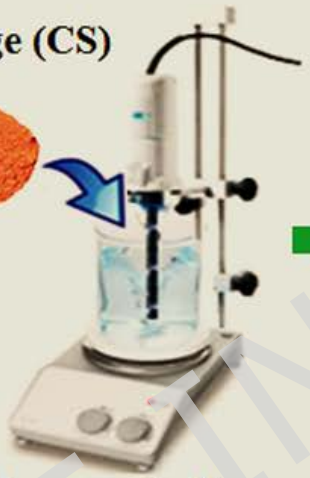
MP MS



Homogenization process for 30 min

Eutectic mixture (MP-MS)

Copper sludge (CS) powder



Homogenization process for 1 h

Direct impregnation process

CC powder



Homogenization process for 2 h



Molding process



leakage test (heating at 45 °C for 30 min)





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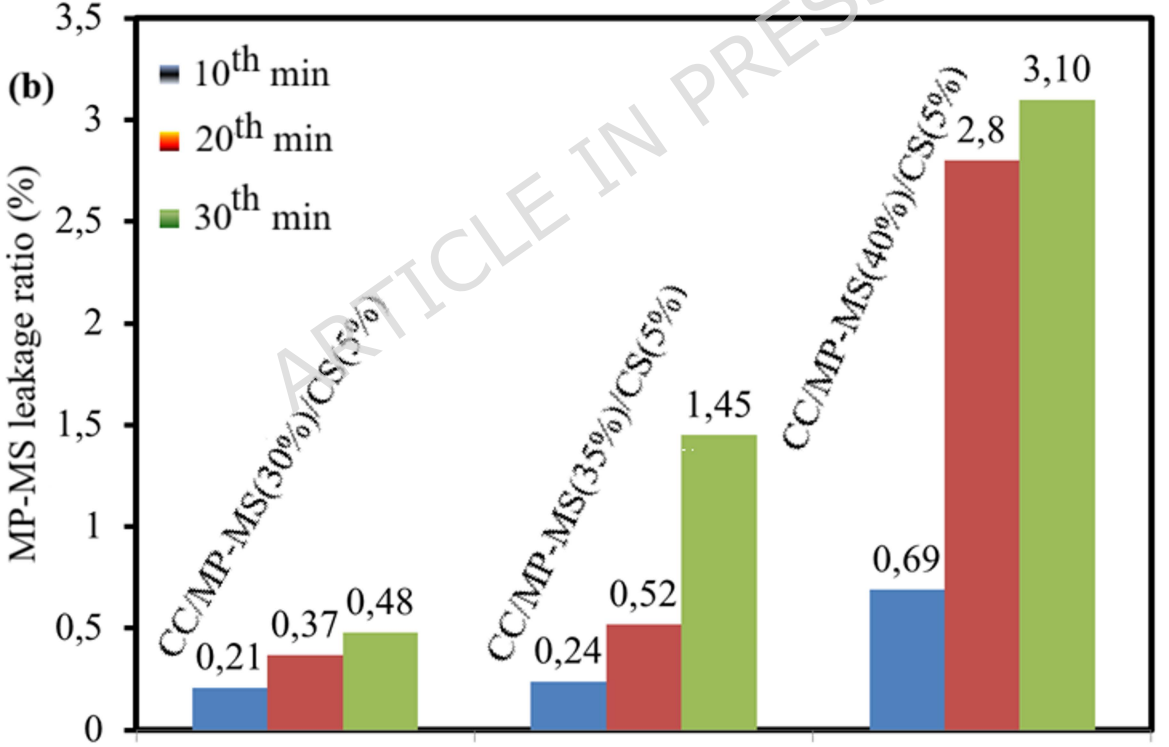
(a)



(b)



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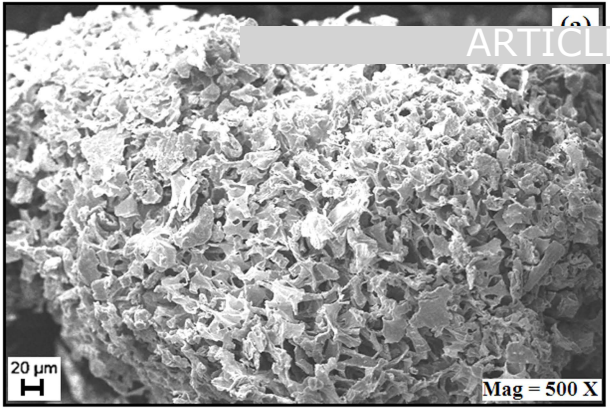

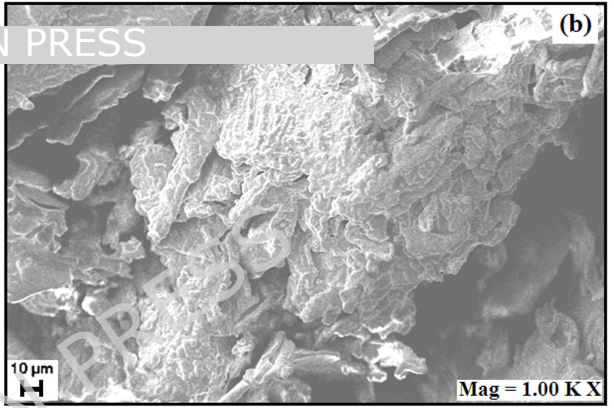

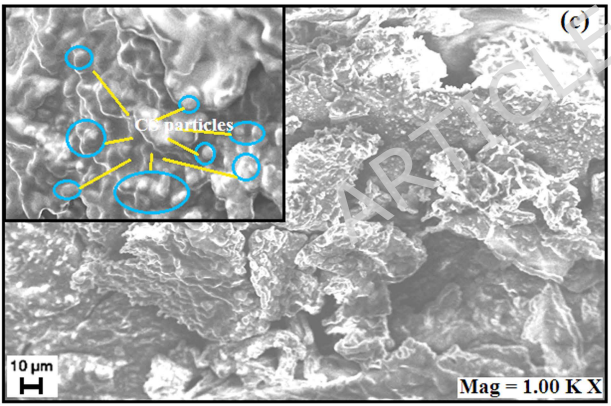

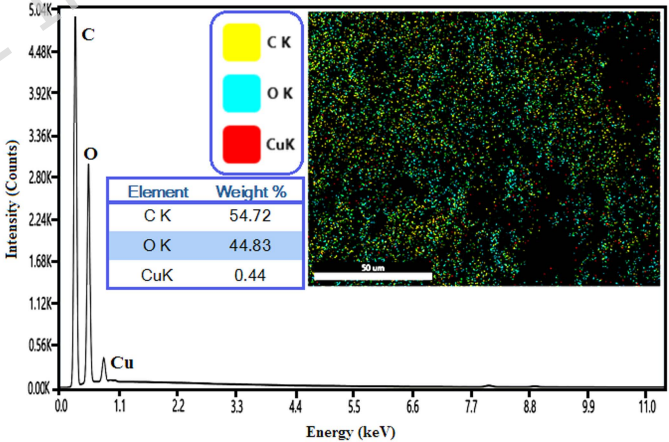

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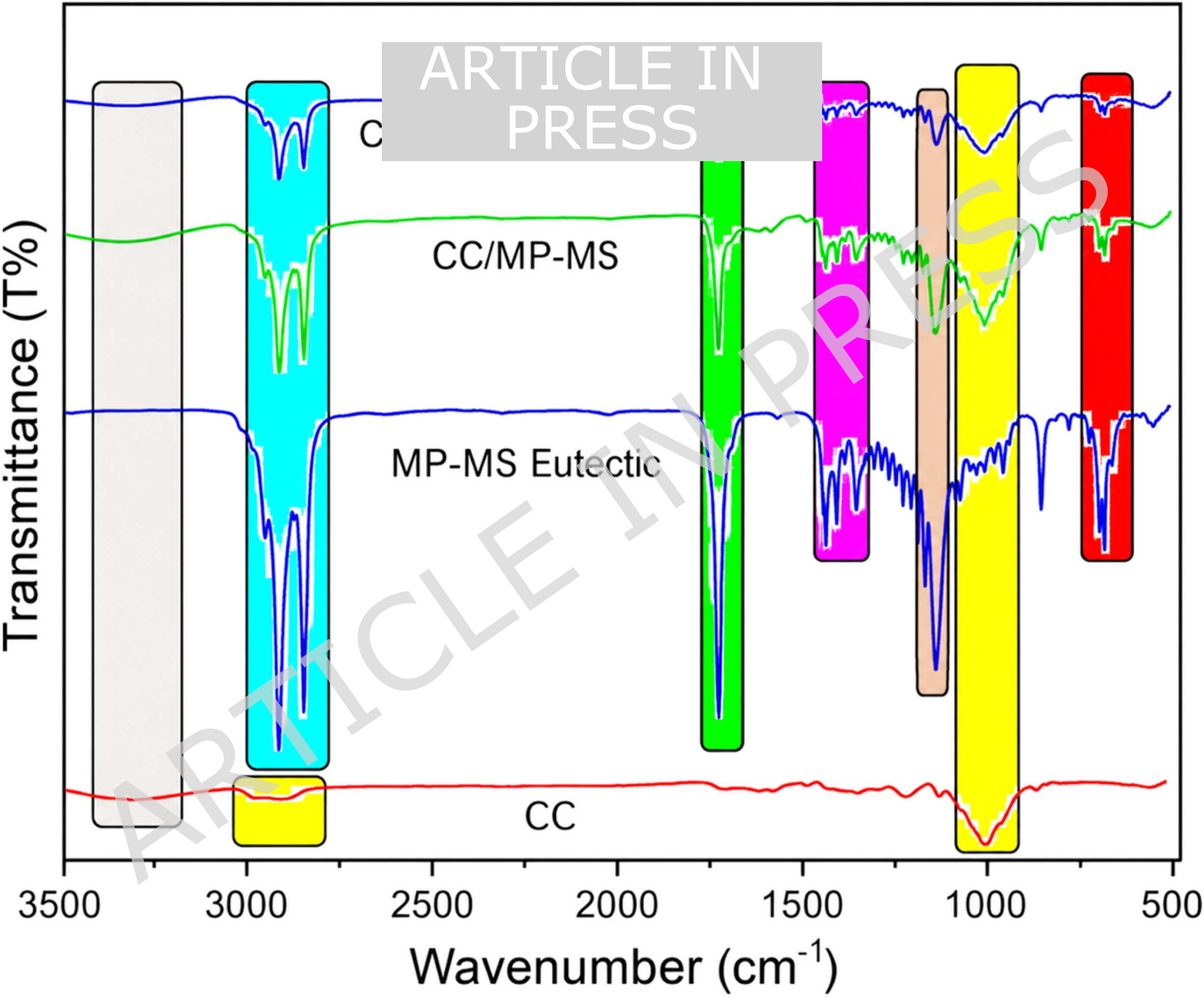

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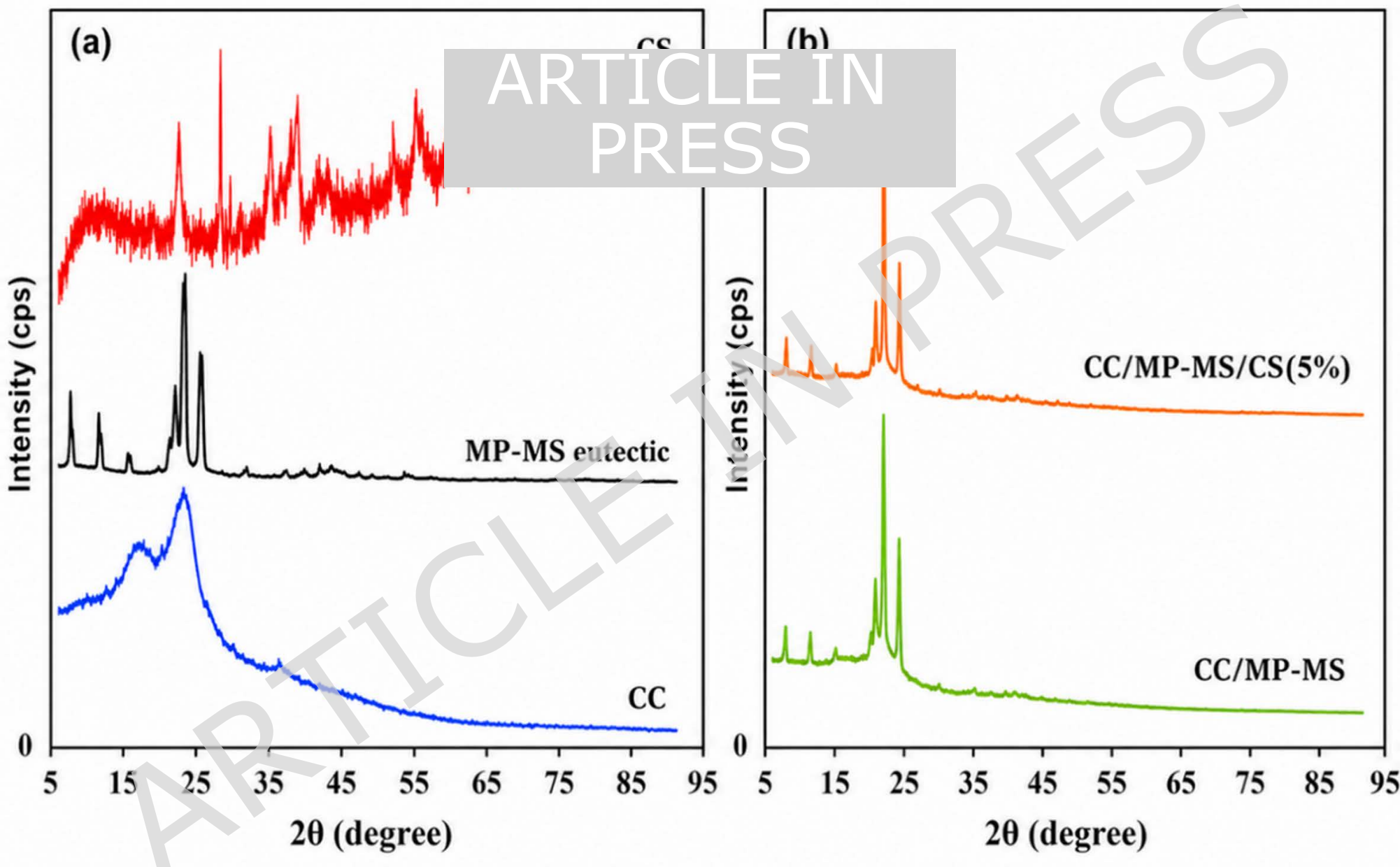

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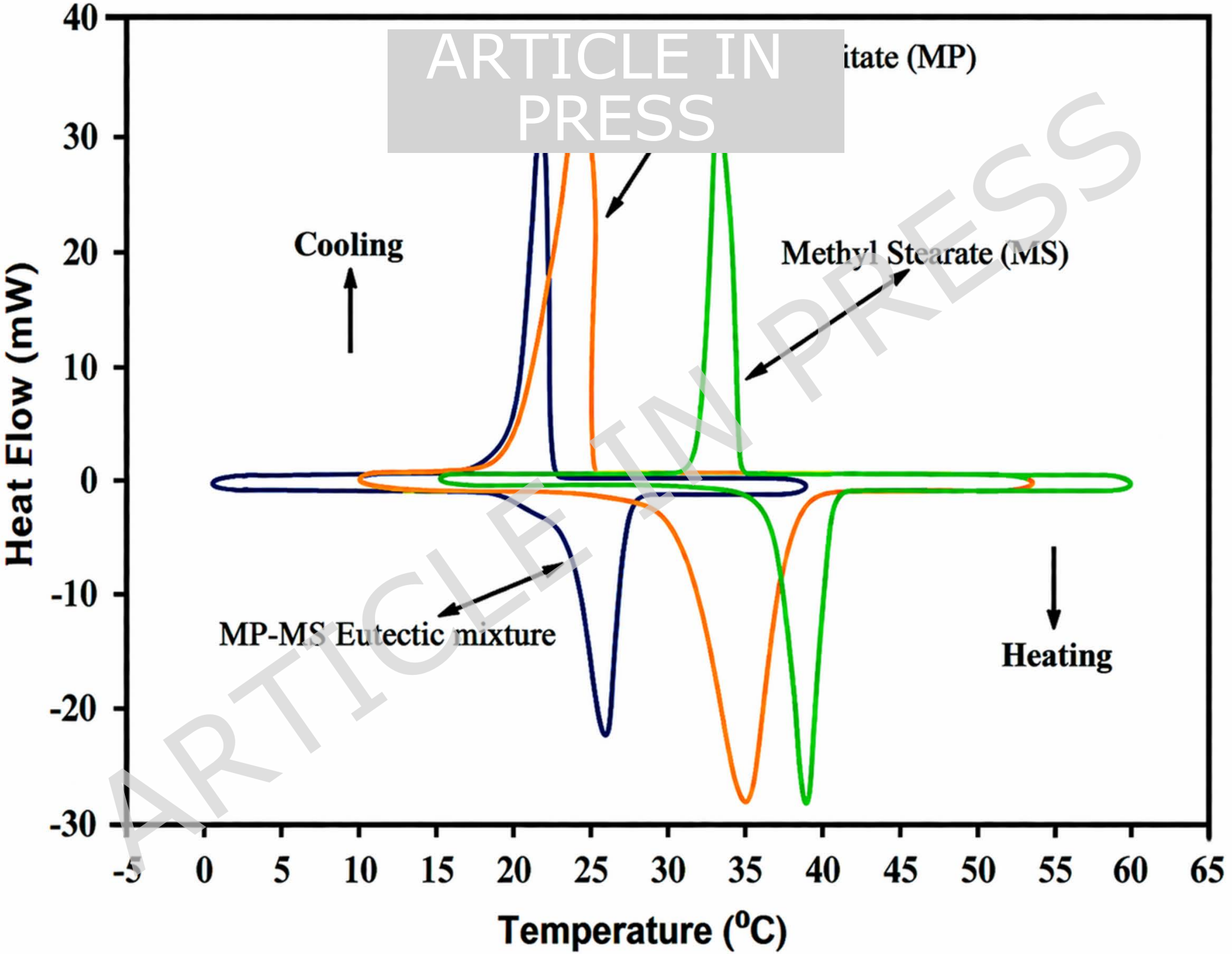

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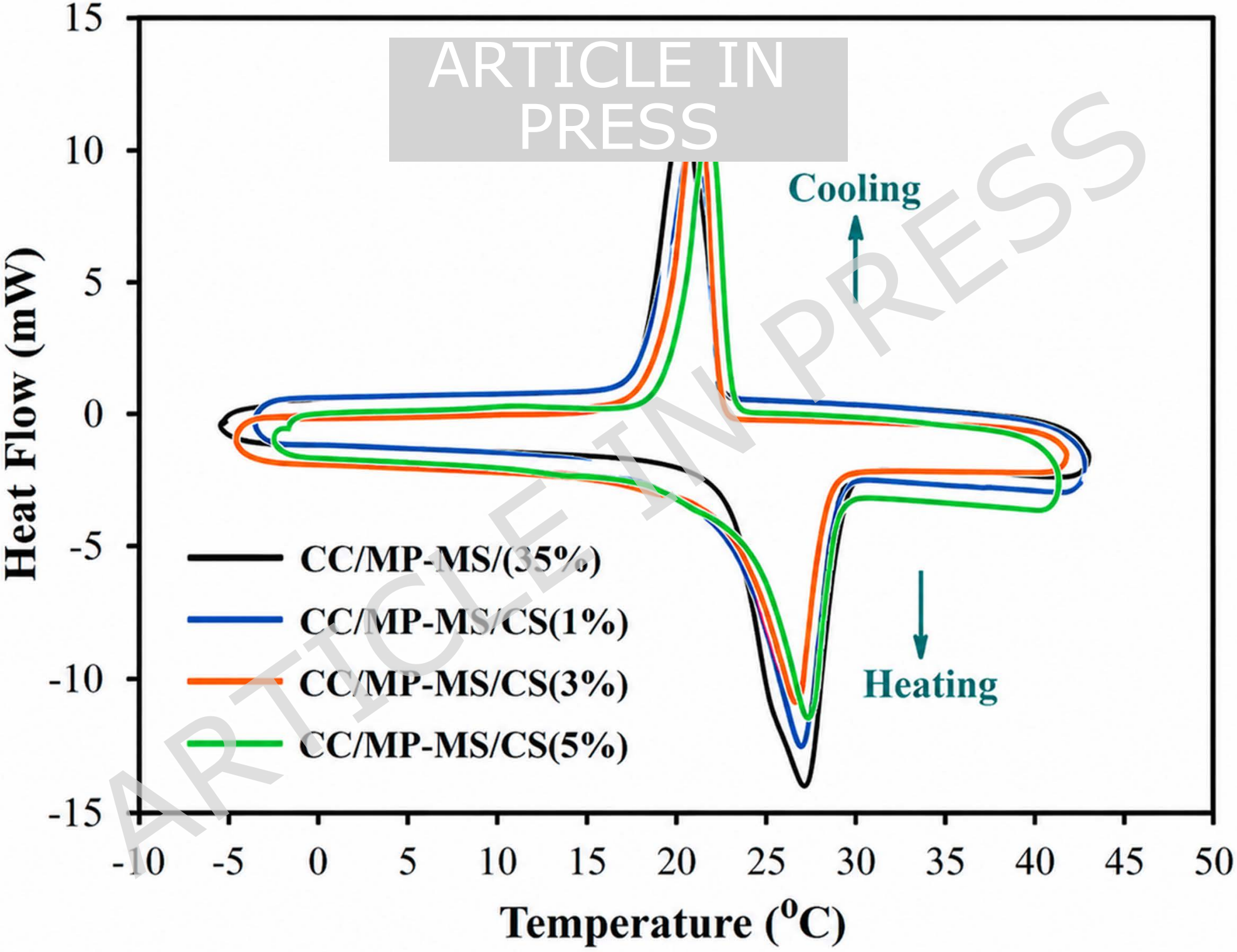

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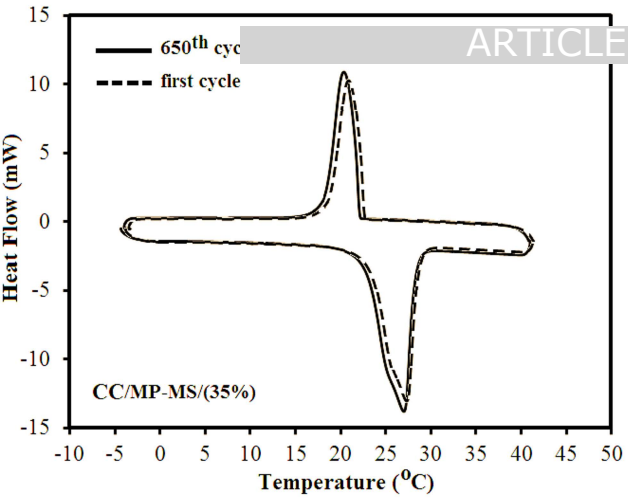

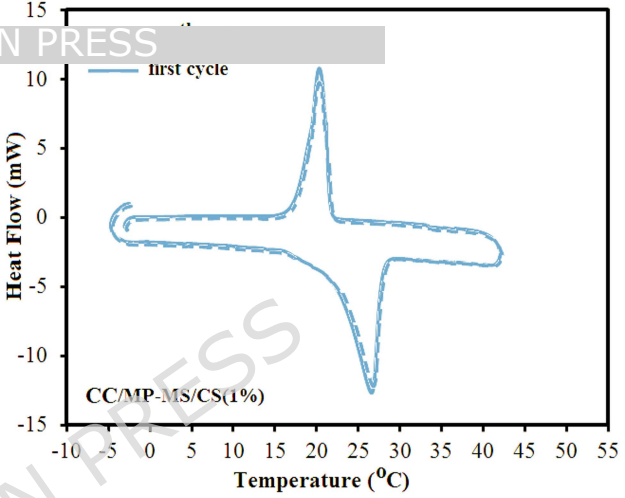

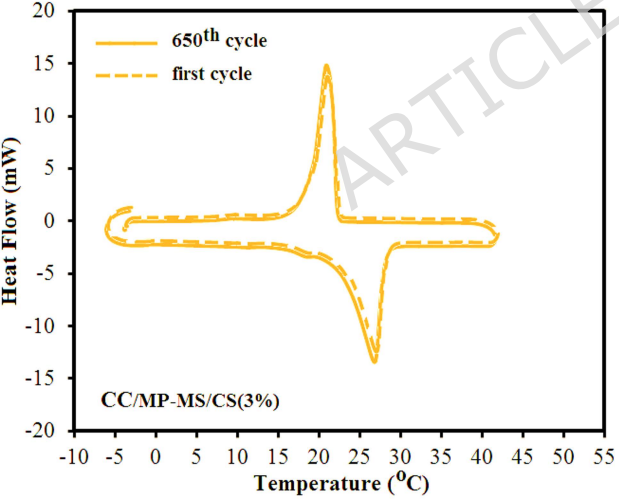

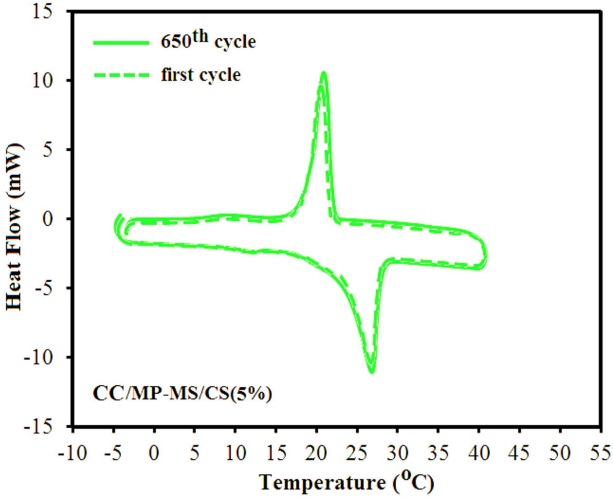

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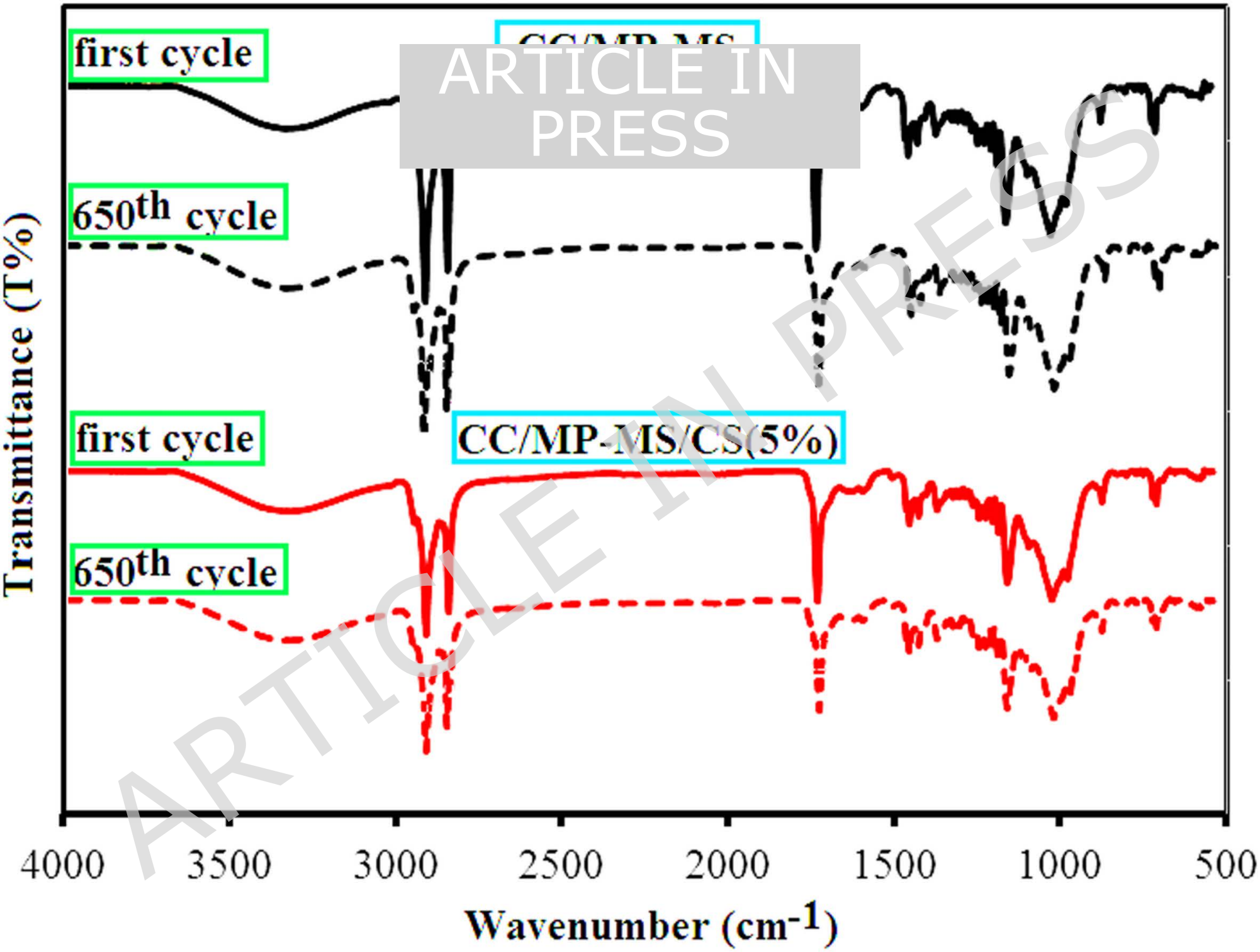

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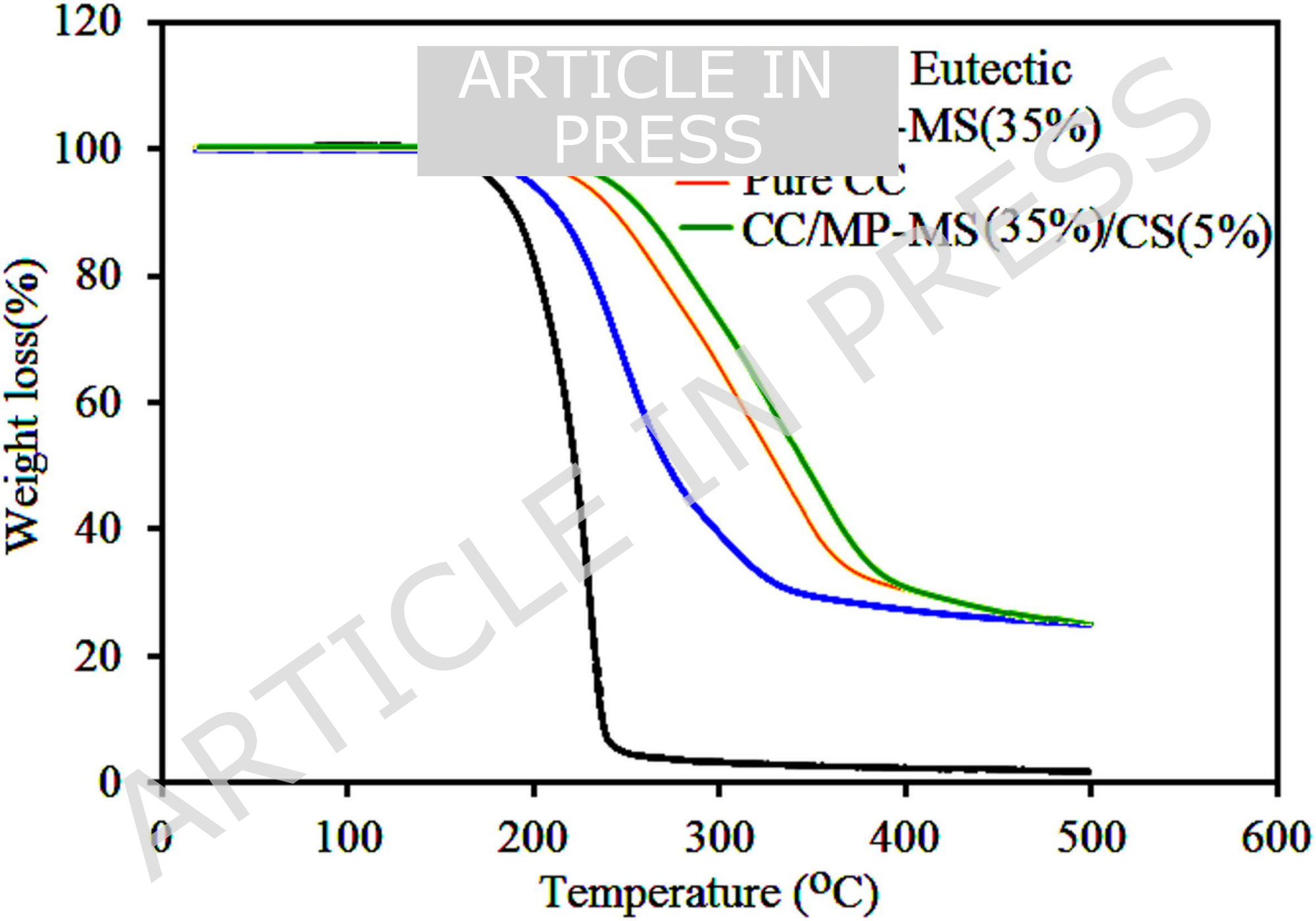

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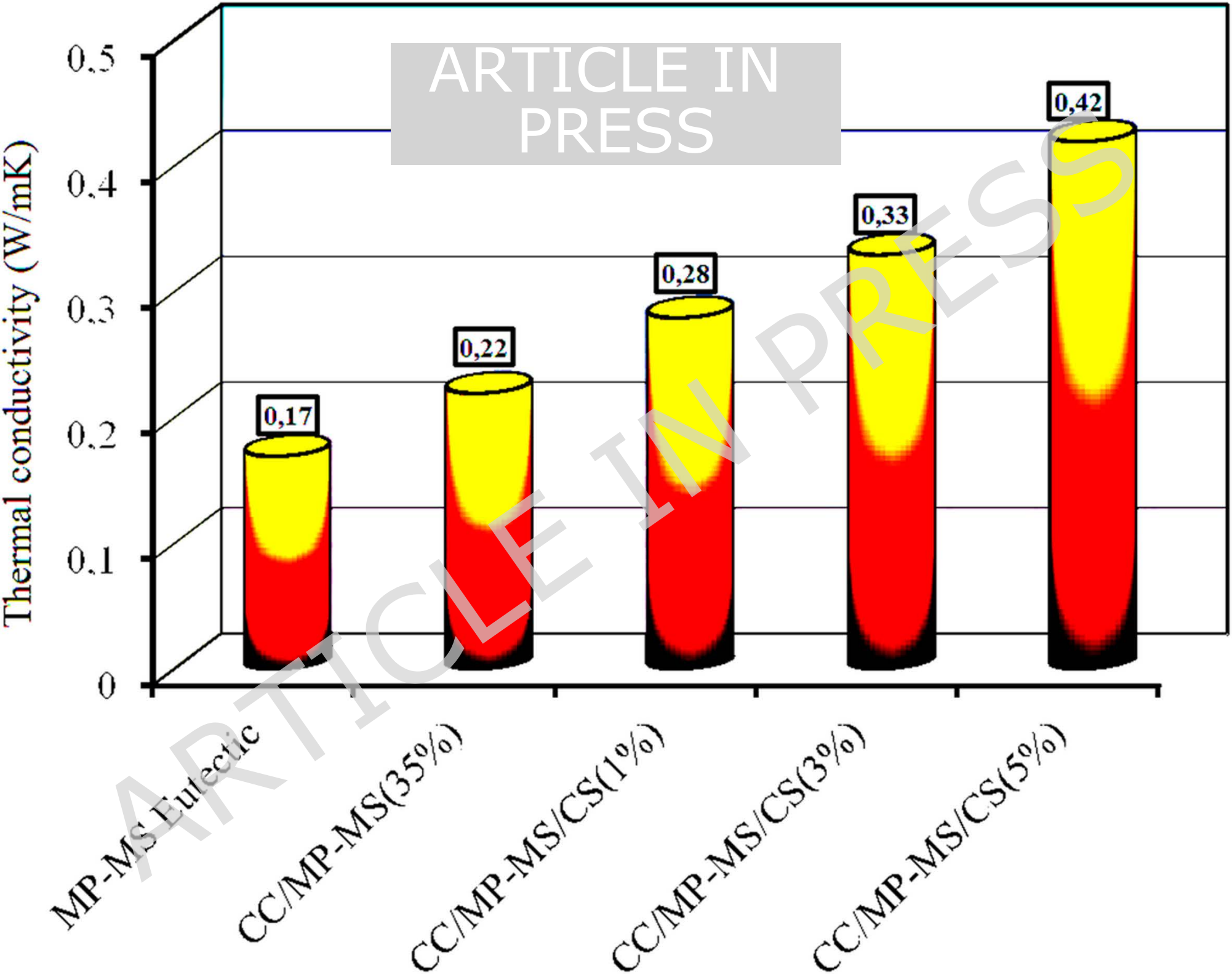

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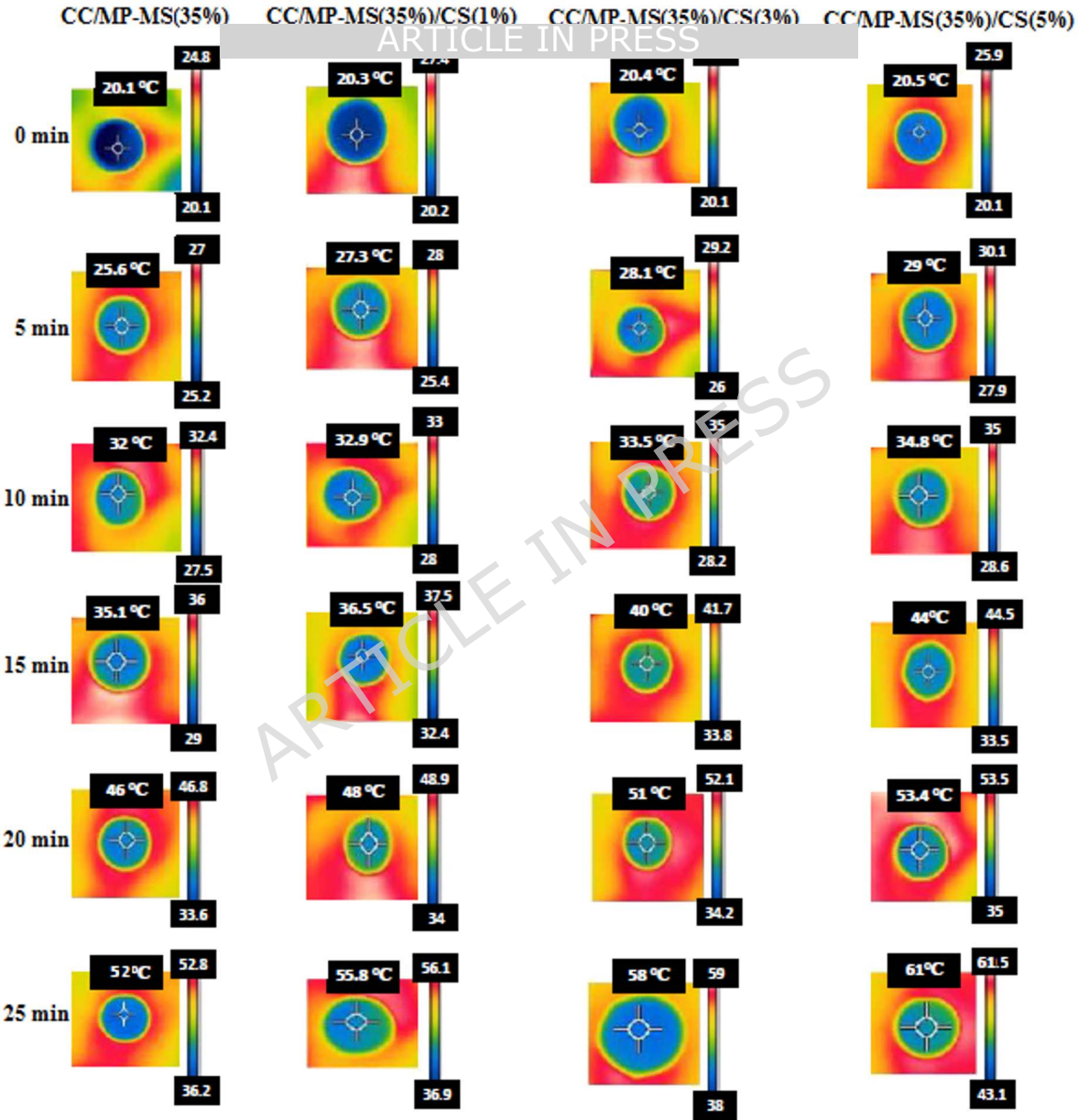

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