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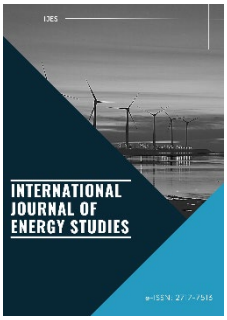

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New boron-containing microcapsule for energy storage with upgraded flame retardant properties

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Highlights

- Novel boron-containing microcapsules were produced as flame retardant materials.
- The changes in the structure property expanded the potential applications of the compounds.
- The synthesis method also allows us to obtain different boron-containing micro/nano capsules.

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ABSTRACT

This study includes encapsulation of a phase change material (PCM), n-octadecane, in boron functionalized polyurethane (PU) shell by interfacial polycondensation method without using cross-linker. Boron is expected to impart flame retardancy to PU based shells. The fact that the boric acid used in the study is abundant and cheap in our country makes the study economically advantageous. This work is noteworthy because it is the only microcapsule study using boric acid rather than ours. In this context, boric acid-containing capsule (TB) and ethylene glycol-containing capsule (T) were produced and compared in terms of latent enthalpy storage capacity, flame retardancy, and some other common specific properties.

Fourier transform infrared (FT-IR) spectrophotometer, differential scanning calorimeter (DSC), thermal gravimetric (TG) analysis, bomb calorimeter analysis, particle size distribution (PSD) analysis and scanning electron microscopy (SEM) were utilized for characterization and purification of thermal resistance of produced microcapsules. The average particle diameter of produced microcapsules is between 13.4-20.0 µm and encapsulation efficiency is also between 28.4 % (68.6 Jg-1) -39.6 % (96.0 Jg-1). Limited oxygen index (LOI) values of TB and T are 20.2 and 18.7. Calorie releases for capsules are 34.6 kJg-1 and 16.7 kJg-1 respectively. N-octadecane is an organic compound and has a high vapor pressure especially at high temperatures. It was clearly seen in this study that its evaporation was prohibited up to 180 °C in PU-boron based shell by encapsulation.

Keywords: Polyurethane, Boron, n-octadecane, Encapsulation

1. INTRODUCTION

Global energy consumption has been increasing at an exponential rate in the past decades, and is expected to undergo a 56% rise by the year 2040. Specifically, the total energy consumption in the 2010s is recorded to be 524 quadrillion British thermal units (Btu). This value is expected to increase to 630 quadrillion Btu in the 2020s, and further to 820 quadrillion Btu in the 2040s [1]. This situation brings different solutions for scientists such as the use of waste materials [2], [3], [4] or microencapsulation [5], [6], [7]. Microencapsulated structures are structures with a core material to be encapsulated and a shell material made of natural or synthetic polymers (Fig. 1).

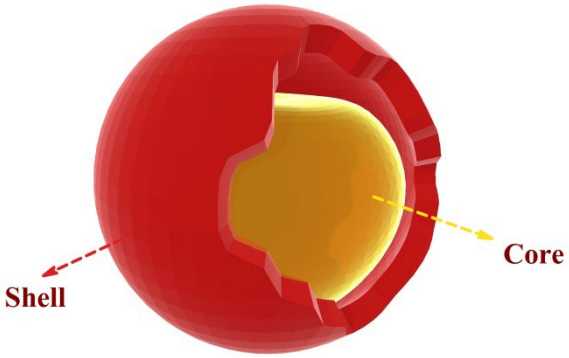

Figure 1. Microcapsule structure

Microencapsulation is used in many fields such as vitamins, paints, antimicrobial materials, hormones, cosmetics, textiles, drug delivery and so on [8], [9]. Compared with inorganic shell materials, microcapsules with polymer shell have attracted many attentions due to their variety, designability, facile preparation, outstanding mechanical strength etc. [10].

Polyurethane microcapsules have been widely used for self-healing composites because they provide good compatibility with various materials and exhibit excellent adhesion to many substances [11]. The polyurethane shell is controllable because of broad possible variations in synthesizing polyurethane and has good mechanical property and high chemical and corrosion resistance in addition to reasonable cost represents an excellent candidate for self-healing applications [12]. They are usually made with four different isocyanates (2, 4-toluendiizocyanate (TDI), 4,4- methylene phenyl diisocyanate (MDI), hexamethylene diisocyanate (HMDI) and isophorone diisocyanate (IPDI)). The selection of reactive monomers as shell material is very important for interfacial polymerization. TDI with good reactivity and endurance property has been wildly used for preparing microcapsules [13]. In literature there are lots of TDI micocapsules;

Hong and Park synthesized a microcapsule wall consisting of TDI/Ethylenediamine (EDA) [14], Haghayegh and et al. obtained PU shell by using TDI /IPDI/TMP [15], de Souza Rodrigues et al. produced polyurethane (PU) microcapsule wall by using TDI/IPDI diisocyanates [16], Sobak et al. synthesized PU shell by using TDI/diol mixture [17], He et. al. synthesized TDI/butandiol shell containing pirimiphosmethyl as core material [18], Cai et al. produced polyurea microcapsule with TDI/diethylenetriamine (DETA) containing dodecanol-dodecanoate as core material [19], Alizedegan et al. synthesized microcapsule wall consisting of TDI/IPDI containing IPDI as core material [20], Du et al. obtained microcapsule containing TDI as core material [21], Ni et al. produced microcapsule possessing TDI/DETA shell [22], Polenz et al. used TDI-polyetheyleneimine (PEI) as shell material for encapsulation [23], Lu et al. synthesized double shell microcapsule by using TDI/polypropylene glycole2000 [24], Ma et al. synthesized PU microcapsule shell by using TDI/IPDI and MDI [25], Watanabe et al. studied with polypropyleneglycol /TDI for PU synthesis [26] and Maruyama et al. syhthesized TDI/triethylene tetramine PU shell [27]. Ethylenediamine, diethylenetriamine, 1,4-butanediol, and PEG1000 were used as reactants to diisocyanates in Pušla's study. It was found that impregnation of orange oil is accelerated when PEG1000 was used, but slower when multifunctional chains such as ethylenediamine and diethylenetriamine are used and mechanical resistance increases [28].

In our previous study, n-octadecane was successfully encapsulated using MDI/phenylenediamine [29] and in this study, the chemical and mechanical properties of polyurethane shells (obtained from TDI) with boric acid and ethylene glycol (EG) that contain n-octadecane as the core material were compared. The data were provided using experimental characterization techniques, such as: FT-IR, DSC, SEM, particle size distribution and TGA to follow the synthesis, characterization, morphology and thermal stability of the microcapsules.

There are no microcapsules with improved thermal properties using boron in the literature. This is because boric acid cannot react easily and disrupts the microcapsule walls. However, this study showed that boron derived from boric acid can be appropriately placed on microcapsule walls. By using boron, the burning of easily flammable polyurethane microcapsules was delayed. In this way, it is aimed to expand the usage areas of polyurethane microcapsules. Another positive aspect of the study is the use of easily available and cheap boric acid as a boron source.

2. EXPERIMENTAL DETAILS

2.1. Materials and Fabricating the Microcapsules

Technical grade boric acid supplied from ETİ Maden Enst. and TDI supplied from Merck was used as monomer. Technical grade cyclohexanone (TEKKIM) was used as solvent and tween20 (Merck) was used as dispersion agent. Dibutyltindilaurate (DBTDL) (Merck) selected as catalyst.

2.2. Procedure for Microencapsulated PCMs Production

The interfacial polycondensation method was used for the encapsulation process. For the production of the capsule with boric acid (TB); TDI and n-octadecane (at an equivalent amount of the wall material) were dissolved in cyclohexanone at a ratio of 1/10 by mass at room temperature as solution 1 (1). Boric acid was dissolved in water at a ratio of 2/3 moles together with TDI separately as a second solution 2 (2). The two solutions (1 and 2) were added dropwise into the solution (200 mL) containing tween 20 (1% by mass) and DBDTL (3% by mass). After the mixture was homogenized for 5 minutes, it was transferred to the mechanical mixer and mixed for another 2 hours at 500 rpm at room temperature. The same procedure was applied for ethylene glycol-including capsule (T) with an equimolar ratio. The microcapsule production method was given in Figure 2.

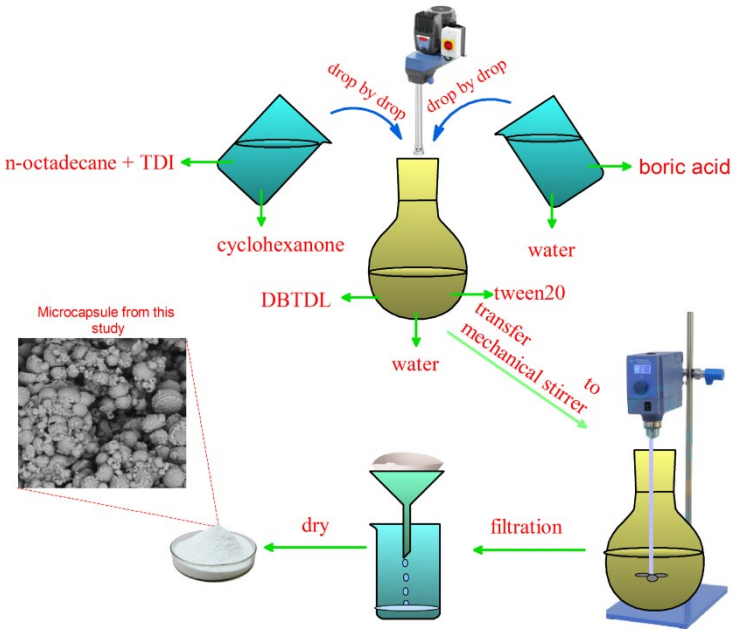

Figure 2. Production of microcapsules with boron

The reaction mechanism is roughly shown in Figure 3. In the mechanizm, the -OH groups of boric acid binded to the isocyanate groups in the dizocyanate allows the polymer to extend from both ends. The high reactivity of isocyanate groups enables the diisocyanate to react with boric acid.

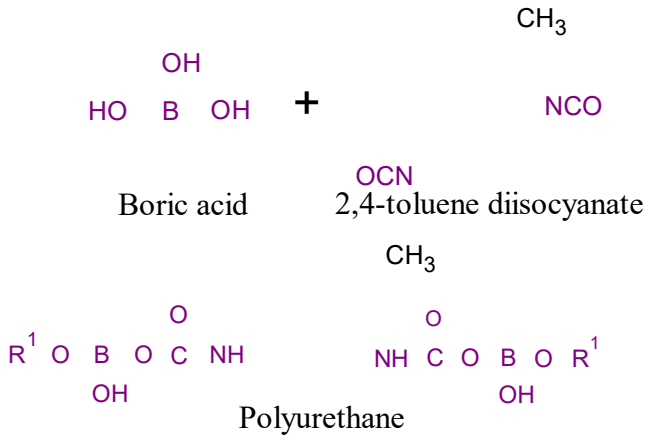

Figure 3. Polymerization reaction of polyurethane with boron

2.3. Methods of Analysis for Microencapsulated PCMs

FT-IR spectroscopy analysis determining the structure was performed using Jasco 430 model spectrophotometry instrument. Thermal analysis for the determination of thermophysical property was performed using a DSC instrument (Netzsch DSC214 Polyma) and thermal endurance limits were applied with the TG Analysis instrument (Perkin Elmer). The surface morphology of the microparticles was analyzed through SEM (Mira3 Tescan) and particle size distributions of microparticles were elucidated by using PSD techniques (Malvern Mastersizer 2000 particle size analyzer). Flame retardancy was studied by a hypothetical curve using adiabatic calorimeter burning time data using the LECO AC350 Adiabatic calorimetry instrument.

3. RESULTS AND DISCUSSIONS

For microencapsulated PCMs, structural characterizations, thermal energy storage performance determinations, morphology evaluations and thermal resistance limits determinations are generally performed. However, hybrid features require some additional characterization studies. The hybrid property evaluated in this study is flame retardancy. Flammability is a more important property than thermal energy storage for most of the applications. For this reason, methodological studies on the flame retardancy of microparticle material have also been important.

3.1. FT-IR Spectroscopy Investigations for Proving the Structure

FTIR spectroscopy plot of synthesized microcapsules and core material is given in Figure 4. Amine (–NH) peak (3300-3400 cm^{-1}) [30] was observed TB and T microcapsules. The formation of the amine peak indicates that the diisocyanate has reacted. Carbon-carbon ($–CH_2CH_3$) peak (2800 - 2900 cm^{-1}) was observed in all samples. The isocyanate (-NCO) [31] peak (2270-2272 cm^{-1}) observed in both capsules may be due to the presence of unreacted isocyanate on the inner surface of the capsule. While the carbonyl group was not observed for OD, a carbonyl peak (1712-1714 cm^{-1}) [32] occurred in TB and T microcapsules. In addition, O-B-O peak (1367 cm^{-1}) [33] was only observed for TB. This indicates the boron-diisocyanate reaction.

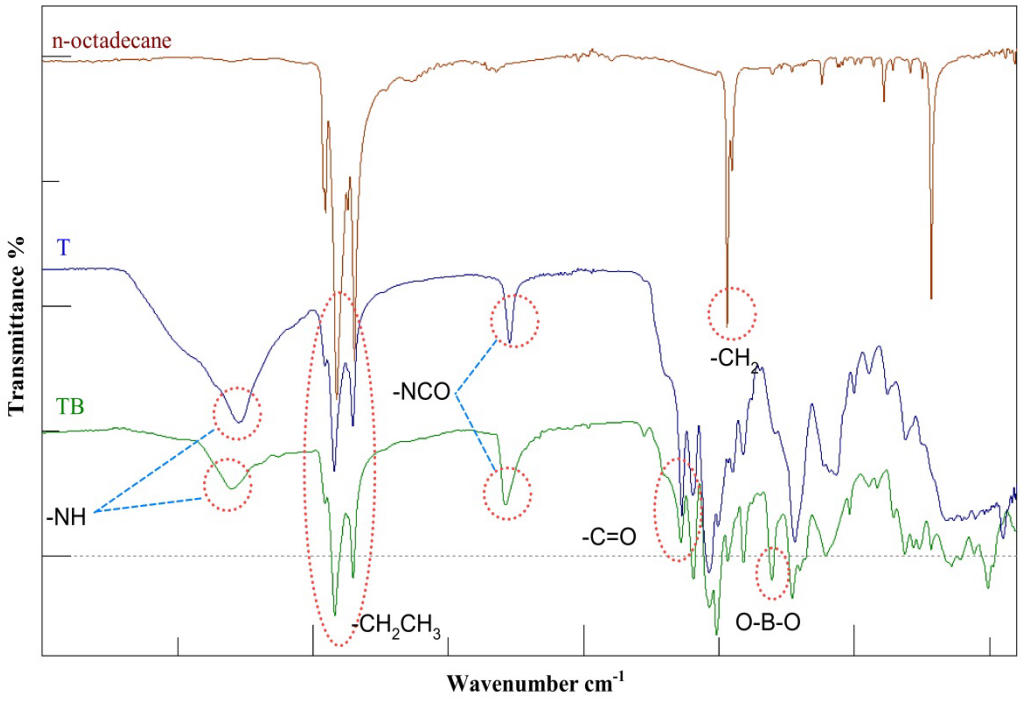

Figure 4. Infrared spectrum of n-octadecane, T and TB respectively

3.2. Scanning Electron Microscopy (SEM) Analysis

According to SEM images (Fig. 5), TB and T microcapsules appear spherical. When the surface morphology is examined, it is seen that a smooth surface is not formed. This is because PU capsule shells usually have a rough surface [25], [34], [35], [36]. Both capsule examples contain broken or cracked capsules because since micro/nano capsules have thin shells, they are not resistant to impacts and pressure. TB appear to be more homogeneous, and the encapsulation rate is better than T. This shows that the addition of boron has a positive effect on spherical capsule formation.

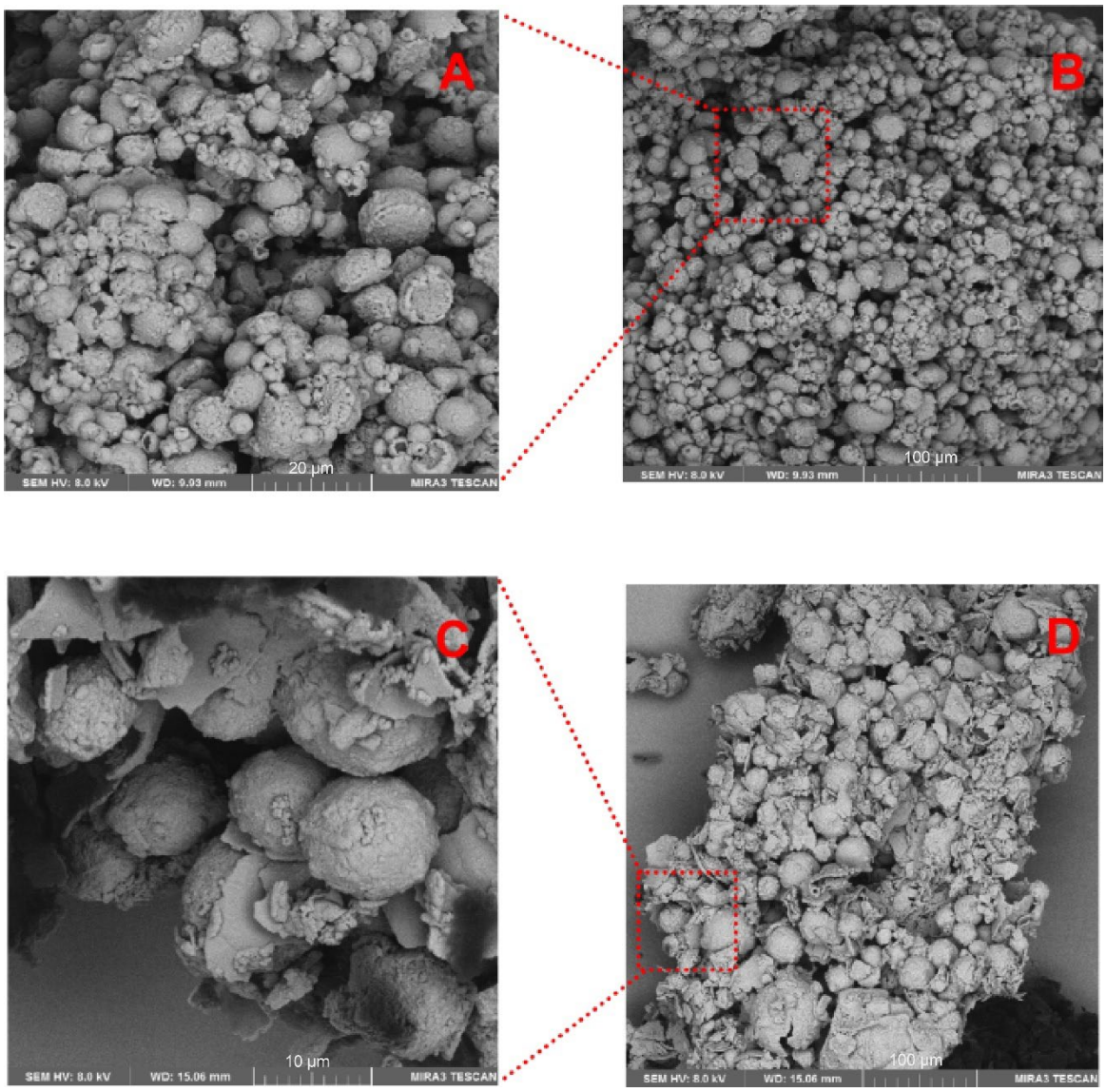

Figure 5. SEM images for A, B) TB and C, D) T respectively

3.3. DSC Analysis for Thermal Energy Storage Property of the Materials

Encapsulation efficiency of microcapsule was calculated by using n-octadecane pure enthalpy value (242.0 Jg^{-1}). n-octadecane encapsulation efficiencies were 39.6 % (96.0 Jg^{-1}) in TB and 28.4% (68.6 Jg^{-1}) in T (Fig. 6). That is, the addition of boron to the toluene diisocyanate capsule caused an increase in latent enthalpy storage. DSC analysis gives information about the impurities of the substances as well as melting and freezing temperatures. While different thermal picks (increases or decreases) that may occur on the graph indicate the deterioration of the material, it also shows the presence of different types of substances. In this study, the heating and cooling thermograms of the capsules did not peak except for melting and freezing.

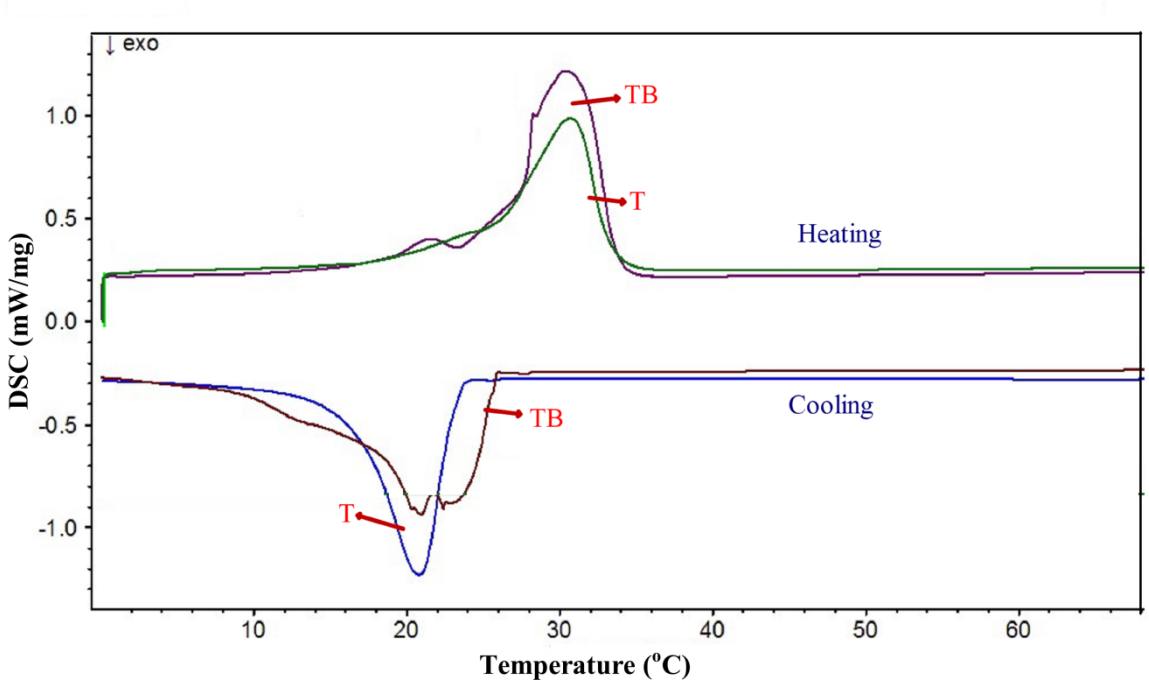

Figure 6. DSC thermograms of TB and T microcapsules

Thermogram data results of some microcapsules containing n-octadecane core material are given in Table 1 as compared to the literature. Although the core material is the same, microcapsules with different melting and freezing temperatures were obtained. Variations in enthalpy values were observed depending on the percentage of core/shell. Enthalpy values also indicate capsule shell thickness.

Table 1. Thermogram data results of some microcapsules containing n-octadecane core material

Study	Shell material	Core material	Melting temperature (°C)	Melting enthalpy (Jg^{-1})	Freezing temperature (°C)	Freezing enthalpy (Jg^{-1})	Encapsulation ratio (%)	Mass yield (%)
This study	T	n-octadecane	25.6	68.64	33.1	64.41	28.4	98.1
This study	TB	n-octadecane	27.6	95.97	33.6	91.39	39.6	98.6
[37]	MAA-MMA	n-octadecane	27-30	111-156	11-16	111-155	46-66	-
[38]	(St-co-DVB-co-AAm)	n-octadecane	21-24	57.9-150.7	22-24	55.1-152.7	22.7-63.1	-
[39]	Polystyrene	n-octadecane	23.3-23.8	141.7-143.7	22.4-23.4	141.4-144.7	58.5-59.4	-
[40]	PMMA	n-octadecane	21.25	143-170	-	-	65.7-78.7	-
[41]	$CaCO_3$	n-octadecane	28.09-29.19	46.93-84.37	23.43-23.54	44.12-82.15	21.89-40.04	-
[33]	Pentafluoro styrene	n-octadecane	28.1-31.9	44.3-171.8	23.9-24.1	43.6-169.3	19.6-76.1	99.1-99.7
[42]	MF/TiO_2	n-octadecane	27.7	120.5	23.8	119.3	50.4	-
[43]	Silk fibroin /TiO_2	n-octadecane	28.42-30.51	85.35-103.89	20.64-20.9	83.07-108.85	34.3-45.0	-

As can be seen from the table, enthalpy values vary. This is due to the amount of core it contains. In the literature, there are microcapsules with different enthalpy values at different percentages. The microcapsules obtained in this study have average enthalpy values.

3.4. Particle Size Distribution (PSD) Investigations

Tween 20 was used as a distribution agent. The absence of a few peaks indicates that the particles are in a similar distribution, which indicates homogeneity. TB and T show homogeneous particle size distribution (Fig. 7). Average particle size (d(0.5)) of TB and T were 13.4 µm and 16.9 µm respectively. The smallest 10% particle size (d(0.1)) and the largest 10% particle size (d(0.9)) were given in Table 2. These results are consistent with the literature [44], [45], [46]. It is clearly seen that boron treatment did not disturb the particle size homogeneity of the microcapsules. In addition, particle distribution graphs were found consistent with the SEM images in Figure 4.

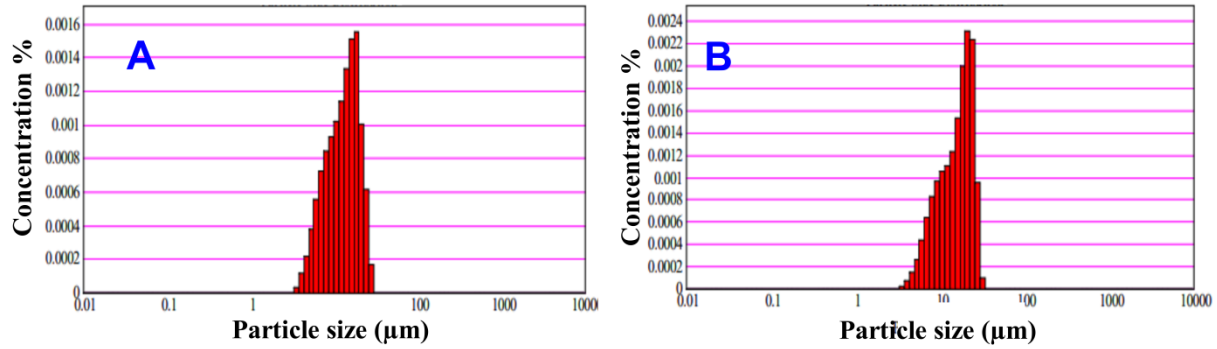

Figure 7. Particle size histograms of A) TB and B) T microcapsules

3.5. Thermal Gravimetric (TG) Analysis

The decomposition temperature of pure n-octadecane was 180 °C [37]. According to Figure 8, Thermal decomposition initiation temperatures for TB and T are 182.7 °C and 181.3 °C respectively. So, thermal decomposition began approximately at the same point for TB and T. However According to the TG graph, a significant increase in the degradation temperature of TB was observed compared to T. This result is compatible with calorimetry and flame retardancy tests.

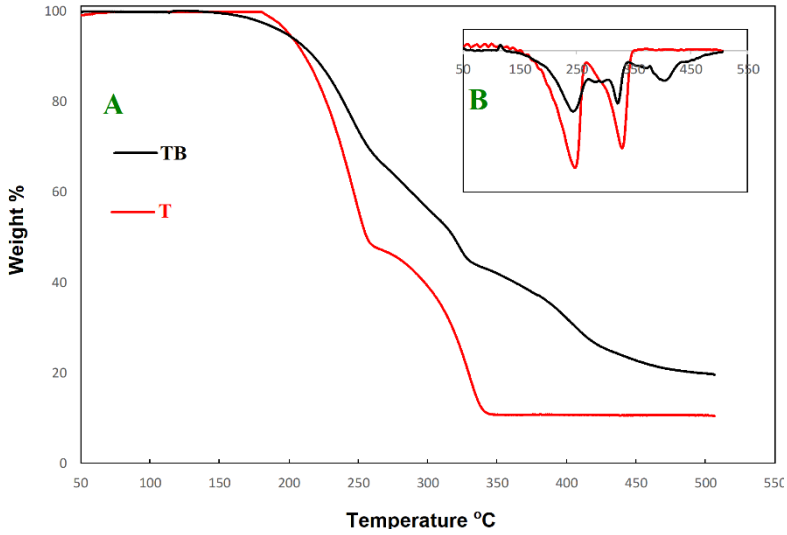

Figure 8. TG thermograms (A) and DTG thermograms (B) of TB and T microcapsules

3.6. Flame Retardancy of Microencapsulated PCMs

Combustion calorimetry is often used to determine the enthalpy of formation of organic compounds containing C, H, O and N atoms, since they are completely oxidizable, and the final state of the combustion reaction is well characterized [47]. The combustion heat of the produced microcapsules was 16,692 Jg^{-1} and 34,595 Jg^{-1} for TB and T respectively. This indicates that the energy released as a result of the combustion of the TB compared to T microcapsule decreases. In other words, the addition of boron to the microcapsule wall material supports the fire-retardant property. Microcapsule bomb calorimetry graph was given in Figure 9 and total thermal results were given in Table 2.

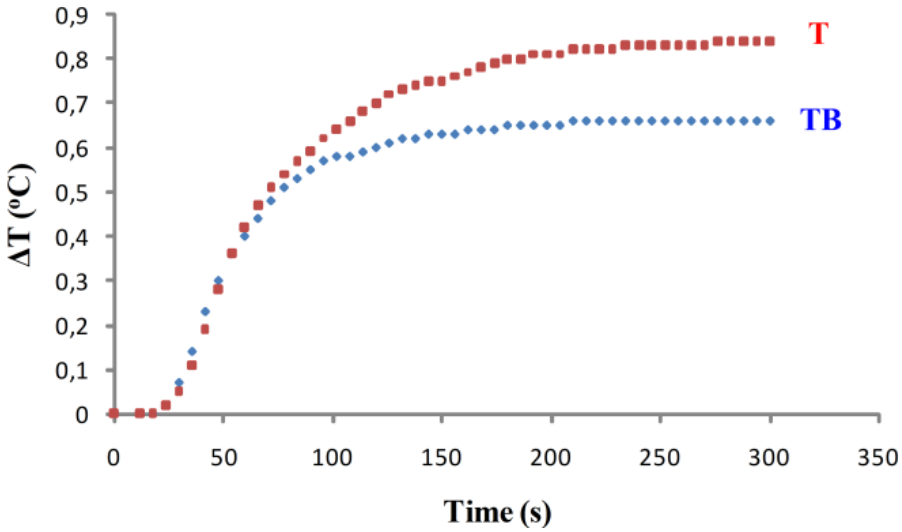

Figure 9. Calorimetric thermograms of TB and T microcapsules

Flame retardant data graph (Fig. 10) was drawn by using polystyrene limited oxygen inex (LOI) (17.6) [48], poly(acrylonitrile) LOI (18.0) [49] and toluene LOI (11.6) [50] values with burning 30 mg sample three times and averaged. The LOI values of the microcapsules were calculated by using equation (y=3.977x-38.32) (1) obtained from the graph. Ignition time was 3 s and burning time for TB and T were 42 s and 36 s respectively. According to the calculations from equation (1), LOI values for microcapsules are 20.2 and 18.7 for TB and T respectively. Boron addition caused an increase in LOI values of microcapsules on account of boron showed fire retardant property.

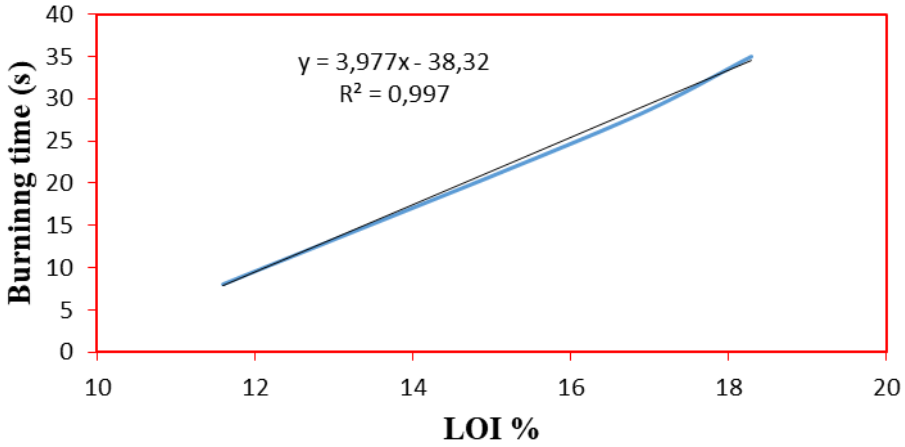

Figure 10. Hypothetical LOI -burning time graph for determination of LOIs of PU and boron-based microcapsules

Total thermal behavior and PSD of microcapsules were given in Table 2.

Table 2. Thermal behavior and particle size distribution of microcapsules

Sample	Decomposition temperature (°C)	Combustion heat (kJg^{-1})	LOI (%)	Particle size distribution (µm)		
				d(0.1)	d(0.5)	d(0.9)
TB	182.7	16.7	20.2	6.5	13.4	21.3
T	181.3	34.6	18.7	7.6	16.9	25.4

As seen in the table, while there was no change in the decomposition temperature of microcapsules to which boron was added, a significant increase in combustion heat values was observed in favor of TB. This situation, supported by the LOI value, proves the positive heat resistance in the

microcapsule to which boron is added. The particle size distribution was observed to be narrower for TB. A narrow particle size distribution is a desired condition for homogeneity in particle size.

4. CONCLUSION

The basis of this study is the production of microcapsules with high thermal resistance and suitable for industrial applications. In this study, the flame retardancy and thermal decomposition properties of the PU-shelled microcapsule were increased by adding boric acid. In addition, the use of boric acid as a boron source caused a relative decrease in the cost of microcapsule production compared to microcapsules produced from isocyanates.

According to the morphological analysis, spherical and homogeneous microparticles smaller than 25 μm (average 13.4 μm and 16.9 μm) were synthesized. Produced particles were investigated through TG, DSC, flame retardant test, and bomb calorimetry analysis. TG analysis revealed that boron added microparticles are thermally more durable than the other shelled microparticles which started to degrade below the thermal decomposition temperatures of PCMs at the core generally. Since n-octadecane decomposes at 180 $^{\circ}$C, the decomposition temperature of the microcapsules was around 180 $^{\circ}$C. DSC investigations showed that the microparticles had a considerable amount of storage density (melting enthalpies of T and TB are 68.64 Jg^{-1} and 95.97 jg^{-1} respectively) and, they also proved high yield and homogeneity during the synthesis. Flame retardancy of the microparticles was studied through a newly developed method and direct flame applications. The method included the time of burning and LOI parameters of well-known compounds. The decrease in the heat of combustion from 34.6 to 14.7 and the increase in the LOI value from 18.7 to 20.2 prove that there is a significant increase in thermal resistance in the capsules with boron added. However, the limit value is theoretically impossible and therefore not aimed. It can be said that boron imparting to the shell is useful to have better flame resistive materials. It was seen that after adding boron, the microcapsules' thermal endurance limit increased, the heat of combustion decreased considerably, and the LOI value increased to a better state. Besides, microparticles with boron were found spherical in shape and stored more latent heat as compared to the similar structure in the literature.

NOMENCLATURE

PCM: Phase change material

PU: Polyurethane

T: Boron-free microcapsule

TB: Boron inclueded microcapsule

LOI: Limited oxygen index

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DECLARATION OF ETHICAL STANDARDS

The author of the paper submitted declares that nothing which is necessary for achieving the paper requires ethical committee and/or legal-special permissions.

CONTRIBUTION OF THE AUTHORS

Timur Paçacı: Performed the experimental studies, analysis and writing of the article.

CONFLICT OF INTEREST

There is no conflict of interest in this study.

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