Research Article

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Various Combinations of Flame Retardants for Poly (vinyl chloride)

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Abstract: Various combinations of zinc borate (ZB), alumina trihydrate (ATH) and magnesium hydroxide (MH) were used to retard the flammability of PVC composite. Flame retardancy of samples were investigated with limiting oxygen index (LOI) test. Further testing was achieved to expose the individual and synergistic effects of flame retardant additives on heat stability, Vicat softening temperature, fusion time, microstructure, mechanical and thermal characteristics. Microstructural and thermal analyses were performed by scanning electron microscopy and TG/DTA respectively. The LOI results showed that, high levels of ZB-ATH combination provided the highest LOI value of 53.4%. Although ZB and its combinations improved the fire performances of composites, they caused a small reduction at tensile strengths. When compared with plain PVC, flame retardant composites had better thermal stability. In addition to the advantages of ZB, when test results were evaluated with a holistic approach ZB-ATH-MH combination was understood to be an effective flame retardant alternative with this research.

Keywords: flame retardant; poly(vinyl chloride); characterization; thermal stability; tensile strength.

1 Introduction

Poly(vinyl chloride) (PVC) is a widely used polymer especially in electrical and communication cables as a covering insulation and in domestic uses such as in window frames, doors, gutters, and house sidings. It has a high level of combustion resistance on the other hand, PVC is not a safe-material because of smoke and toxic

gas (chlorine compounds, benzene and other aromatics) production characteristic while burning.

PVC actually retards fires both from starting and from spreading because of its flame-retardant nature. Not only the presence of chlorine within the polymer matrix, but also formation of a carbonized product as a consequence of rapid evolution of hydrogen chloride provides a protection from fire [1]. A carbonized product is believed to have both conjugated and crosslinked structures, which protect the polymer main chain while burning. PVC is a thermally unstable polymer and stabilization is required for processing. However, the higher level of “processing aid” and “impact modifier” addition to PVC causes the less flame-resistancy in the formulation [2]. The elements which are interrelated to flame-retardancy of polymers are boron, aluminium, phosphorus, antimony, chlorine and bromine [3]. The usage of these elements in polymers may remarkably affect the thermal, mechanical and electrical properties of the mixture [3,4].

The chemical compounds such as metal alloys, coordination compounds, inorganic and organic compounds are preferred as flame retardants for PVC [5-8]. Inorganic fillers which are alumina trihydrate (ATH) and magnesium hydroxide (MH) play a dual role as flame retardancy and mineral reinforcement [9]. ATH and MH are relatively inexpensive and non-toxic additives on the other hand, their high levels for adequate flame retardancy often lead processing difficulties [10]. Boron-based flame retardants like zinc borates (ZB) carry some advantages. Due to the formation of a glassy protective layer by these additives at the condensed phases, the contact of unburnt polymer and flame region additionally the diffusion of the flammable gases occurred during combustion are impeded [11,12].

In this research, various amounts of zinc borate, alumina trihydrate and magnesium hydroxide were selected as flame-retardant and their incorporation with PVC was investigated. The performances of the flame-retardants on PVC composites were determined in terms of Limiting Oxygen Index (LOI), heat stability, Vicat softening point, mechanical and thermal properties. The main

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novelty of this study is, not only a comprehensive look to a commercial PVC product from the results of the applied tests but also an understanding of the synergistic effects of binary and triple combinations of flame-retardants in composite containing different types of additives. In this study, commercial PVC formulations comprise more than 6 different additives therefore the flame retardance of PVC composite is a complex issue and, here it was aimed to balance physical properties, thermal stability and flammability.

2 Experimental programme

2.1 Materials

Poly(vinyl chloride) (PVC) was obtained from Mexichem Speciality Compounds Inc., USA. Heat stabilizer (Akdeniz Chemical Industry and Trade Inc., Turkey), acrylic impact modifier (Shandong Rike Chemical Co. Ltd., China), polyethylene wax (Empisan Chemistry Industry Co., Turkey), pigment-TiO₂ (Shandong Dawn Titanium Industry Co. Ltd., China) and CaCO₃ filler (Anadolu Micronize Mining Industry and Trade Inc., Turkey) were used to prepare the mixture. As flame retardants alumina trihydrate (Al(OH)₃), magnesium hydroxide (Mg(OH)₂) and zinc borate (2ZnO.3B₂O₃.3.5H₂O) were supplied from Eti Aluminium Inc. (Turkey), Bereket Chemistry Medicine Technic Trade Inc. (Turkey) and Melos Inc. (Turkey) respectively.

2.2 Sample preparation

2500 g PVC, adequate amounts of additives and flame retardants (based on PVC amount) were mixed using a mechanical mixer (Der-San LB-20) (Table 1). The temperature was set to 112°C and mixer was started operating at automatic mode. When the heater mixer temperature increased to 112°C, the bottom plug opened and the compound was automatically loaded into the cooler mixer. After left in the cooler for about 3 minutes, the compound was unloaded. PVC composites were prepared using a co-rotating twin-screw extruder. Zone temperatures of extrusion were increased to 180-185-190°C respectively, and 50 rpm screw speed was applied. At each formulation PVC samples with a sheet thickness of 1.2±0.1mm were obtained with the mold located at the end of the extruder. Torque values ranged from 11.5 to 13.3 Nm and melt pressures were approximately 6.5 MPa.

2.3 Limiting Oxygen Index (LOI) test

The limiting oxygen index (LOI) is the minimum oxygen concentration that supports combustion of a sample. When the measured value of LOI is high, the fire retardancy is also great. The LOI test is usually used for the comparison of the flammability of polymeric materials and for quality control purposes. In this study, ASTM D2863 standard test method [13] was used for determining LOI value of PVC composites possessing different amounts and combinations of flame retardants.

2.4 Mechanical tests

Mechanical properties of the PVC samples were determined in terms of “tensile strength” and “elongation at break” according to ISO 1421 [14] with a JINGMI WDT-W testing machine at room temperature. The operation was performed at 50 mm.min⁻¹. The tensile strength and elongation at break values of samples were calculated with the expressions given below:

$$\text{Tensile strength} = \frac{\text{load at break}}{(\text{original width}) \times (\text{original thickness})} \quad (2.1)$$

$$\text{Percent elongation} = \frac{\text{elongation at rupture} \times 100}{\text{initial gage length}} \quad (2.2)$$

2.5 Thermal properties

TG/DTA analyses of the composite samples were performed using a Perkin Elmer Diamond TG/DTA thermal analyzer. The measurements up to 600°C were achieved under N₂ flow. A uniform heating rate of 10°C/min was applied during the measurements. The system automatically converts DTA (mV) signals to DSC (Differential Scanning Calorimeter) units (mW) based on the heats of melting of high purity metal standards. Vicat softening temperature test was applied to composites according to TS EN ISO 306 standard [15]. The temperature at which a needle with a diameter of 1 mm² can enter the material under 10 N force is called the “vicat softening temperature of samples”. Besides these tests, fusion time of PVC composites were also determined in the banbury mixer which was located instead of extruder. The operating conditions were 40 rpm and 195±0.1°C.

2.6 Oven heat stability test

Oven Heat Stability test was performed with the procedure described in ASTM D2115-04 [16]. According to the procedure, the relative thermal stability of sheet or molded PVC compounds were determined as discoloration due to exposure to an elevated temperature at controlled oven conditions. PVC sample was divided into 3 pieces. All of the pieces were placed in an oven at 180 °C. Colour measurements of the pieces were achieved by using a spectrometer (Konica Minolta CM-A145) at the time intervals of 10 minutes.

2.7 Surface Morphology

The morphologies of PVC samples were investigated by Scanning Electron Microscopy (FlexSEM 1000) under high vacuum and without metal coating.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results

3.1 Characterization of PVC composites based on flame retardancy

With the Limiting Oxygen Index test results, characterization of PVC composites were achieved in terms of flame retardancy. Table 1 shows the flame retardant content of each sample based on the PVC amount (phr stands for parts per hundred parts of polymer) and LOI values of samples. From Table 1, it is seen that addition of flame retardants cause an increase in LOI comparing with plain composite (PVC0). On the other hand, higher results were obtained when ZB-ATH combination (at the 10 phr total level) and individual ZB (at the 5 phr level) were added to samples. ZB carries an important functionality against flammability and loses its crystalline water during fire. Therefore, released water dilutes the flammable gases, and acts as a heat sink, decreasing the temperature at the burning zone [17]. In another research, Ning and Guo reported that, the LOI of PVC/ZB-ATH was much higher than that of PVC/ZB and PVC/ATH [18]. Table 1 also shows the synergistic effects of binary combinations of flame retardants on LOI values namely; ZB addition to PVC2 (2 phr ZB+3 phr ATH), PVC3 (5 phr ZB+5 phr ATH) and PVC6 (2 phr ZB+3 phr MH) caused high flame retardancies compared to individual usage of MH (PVC4) and ATH (PVC

Table 1: Limiting Oxygen Index test results of PVC composites.

PVC Composite Code	Flame retardant type and level (phr)			LOI value
	ZB	ATH	MH	(%)
PVC0	-	-	-	43.9
PVC1	5	-	-	51.9
PVC2	2	3	-	49.9
PVC3	5	5	-	53.4
PVC4	-	-	5	44.9
PVC5	-	5	-	46.5
PVC6	2	-	3	47.8
PVC7	2	2	2	48.6

5) in composites. Additionally, multiple synergistic effects were observed in PVC7 due to ZB-ATH-MH and it can be mentioned that, this composite is also a good alternative to its counterparts like PVC4, 5 and 6.

3.2 Mechanical properties

Mechanical tests were achieved on PVC composites, Figure 1 and Figure 2 were prepared from the test data. According to Figure 1, plain PVC has the highest tensile strength. The addition of ZB alone (PVC1) and with other flame retardants (PVC2,3,6 and 7) decreases the tensile strengths of composites. It was thought that, inhomogeneous ZB distribution and formation of ZB agglomerates cause weak zones in composite structure [17]. When the results of PVC1 (34 MPa) and PVC3 (32.8 MPa) are compared, it is seen that the increment of ZB amount in composite decreases the tensile strength of the sample. This can be a supporting outcome for the discussion made above. Moreover, although the individual ATH addition causes a high tensile strength (39.2 MPa) the synergism of ZB-ATH at high and low levels (PVC3 and PVC2) negatively affects the composite mechanical behaviour. Besides, this approach is not true for ZB-MH synergism (38.8 MPa) when it is compared with individual MH (37.8 MPa) result. Additionally, the multiple combination of ZB-ATH-MH (PVC7) overcomes the negativity at tensile strength and gives better result than PVC2 and PVC3. It can be concluded that, individual ATH, individual MH, ZB-MH and ZB-ATH-MH addition as a flame retardant to PVC provides close results with plain composite.

When Figure 2 is examined, it is seen that composites containing ZB (PVC1,2,3,6) exhibit better elongation values

Figure 1: Tensile strengths of PVC formulations without flame retardant and with ZB, ATH and MH.

Figure 2: Elongation at break values of PVC composite samples.

than other flame retardant composites. In a previous research, composites prepared with ZB had higher tensile modulus compared to neat PET and higher modulus value of the additive was the reason of this result [17]. All of the elongation at break values are less than plain composite on the other hand, individual ATH (PVC5), individual MH (PVC4) and ZB-ATH-MH synergism (PVC7) give the lowest values. The decreased elongation at break may be due to the higher degree of brittleness introduced by the incorporation of inorganic flame retardants and fillers into the PVC matrix.

3.3 Thermal characteristics of PVC composites

Effects of individual ZB and multiple ZB-ATH-MH contents on TGA thermogram of PVCs are given in Figure 3. From Figure 3 it can be expressed that, the thermal degradation occurs in two stages. The thermal degradation in the first

(a)

(b)

Figure 3: Effects of individual ZB and multiple ZB-ATH-MH contents on (a) TGA thermograms, (b) derivative weight loss of PVC samples.

stage is mainly due to the evolution of hydrogen chloride. ZB containing bound 3.5 mol water removes at 250°C [19]. ATH starts to decompose in the range 180–220°C with the formation of 3 mol water and 1 mol alumina. It was reported to have thermal stability up to 220°C and phase transition from $\text{Al}(\text{OH})_3$ to Al_2O_3 between 250°C and 320°C [20]. Besides, between 280–460°C the degradation of cross-linking and/or degradation of polymeric backbone takes place (i.e. scission of the PVC main chain) [21].

Incorporation of small amounts of individual ZB reduces the thermal decomposition temperature in the first stage while multiple ZB-ATH-MH increases as shown in Table 2. Second stage thermal degradation is related to the cyclization of conjugated polyene sequences to form aromatic compounds [18]. Second stage thermal decomposition temperature and amount of char residue increase with individual ZB and multiple ZB-ATH-MH.

It is observed that, PVCs containing individual ZB and ZB-ATH-MH combinations exhibit better thermal stability

Table 2: Thermal Gravimetric Analysis results of PVC samples.

Sample	Remaining mass (%)		Char Residue (%)
	280 °C	460 °C	600 °C
PVC0	77.3	40.0	29.2
PVC1	75.1	44.1	34.0
PVC7	77.8	43.4	32.9

Table 3: Differential Thermal Analysis results of PVC composites.

Sample	T _{peak} (°C)	Heat of degradation (kJ/kg)
PVC0	271.6	597.9
PVC1	261.2	355.8
PVC7	273.3	166.9

in terms of remaining mass and char residue percent up to 600°C. On the other hand, plain PVC shows thermal degradation at much lower temperatures and more weight loss with temperature.

Figure 4 shows the DSC curves of PVC samples. The degradation of PVC is an endothermic reaction (Table 3) because the degradation process consists of elimination reactions and takes place as reverse to the organic addition reactions that can occur into the double bond of alkenes [22]. The degradation peak temperatures and heat of degradation of PVC samples were presented in Table 3. Individual ZB reduced the degradation peak temperature whereas multiple ZB-ATH-MH content increased. Both individual ZB and ZB-ATH-MH combination decreased the heat of degradation of PVC.

PVC is a cost-effective plastic whereas its low heat resistance causes some challenges to use in different areas. Most PVC products are recommended for operating temperatures of 60 to 65°C (peak temperatures of up to 80°C) because at higher temperatures it begins to soften [23]. In this part, Vicat softening temperatures were determined to understand the effects of flame retardants to PVC composites. From Figure 5 it is seen that, the difference between the softening points of flame retardant composites and plain composite are not big. It is a desired result due to the restricted operating temperatures of PVC. When plain PVC composite is taken into consideration, individual MH (PVC4), individual ATH (PVC5), ZB-MH (PVC6) and ZB-ATH-MH (PVC7) combinations caused a small decrease at softening temperatures. On the other hand, individual ZB (PVC1) and high levels of ZB-ATH combination (PVC3) partially increased the softening temperature of composites.

Figure 4: Effects of individual ZB and multiple ZB-ATH-MH contents on DSC curves of PVCs. **Figure 5:** Effects of individual, binary and multiple combinations of flame retardants on PVCs' Vicat softening temperatures.

The fusion characteristics of PVC composites were investigated as “fusion time”. Fusion time is the time from the point of loading to the point of maximum torque [24]. It was determined for PVC samples at the processing temperature of 195±0.1°C. In order to obtain better mechanical properties, the grain boundaries of PVC must be eliminated and part of the microparticles must be destroyed so that they can be compacted. During further interfusion of the PVC, the boundaries between the submicroparticles disappear, and this is known as gelation, or fusion [25].

In this part PVC processing temperature was selected as 195±0.1°C because it affects the degree of PVC gelation. If the processing temperature is too low, the degree of gelation (or fusion) is reduced. When the opposite takes place, degradation of PVC is observed. Table 4 presents the fusion time values of plain PVC and the flame retardant composites. The lowest fusion time was obtained when ZB-ATH-MH combination (PVC7) was used in composite. ZB-ATH-MH synergism helped the formation of the gelled

Table 4: Fusion time values of plain PVC and the flame retardant composites.

Sample	Fusion time (s)
PVC0	67
PVC1	67
PVC2	73
PVC3	60
PVC4	61
PVC5	63
PVC6	61
PVC7	58

Table 5: The colour change of composites obtained from the oven test.

Time (min.)	ΔE	PVC0	PVC1	PVC2	PVC3	PVC4	PVC5	PVC6	PVC7
10	0.88	0.61	1.07	0.71	1.23	0.88	0.77	0.91	
20	2.08	1.08	1.62	1.10	2.57	1.67	1.52	1.69	
30	3.15	1.89	1.91	1.63	2.40	2.31	2.97	2.24	

state of PVC faster which means that grains fuse quickly together during melting. On the other hand, higher levels of ZB-ATH (PVC3), individual MH (PVC4), individual ATH (PVC5) and ZB-MH combination (PVC6) caused lower fusion time compared with plain PVC composite. At these samples, less energy is required due to the quick fusion of the particles as mentioned in literature [26].

3.4 Heat stability of PVC composites

Heat stability tests on PVC compositions and products carry importance in the practical contexts of processing and service. The method followed here shows the change of coloration in static conditions (standard oven aging) and the time to reach the dramatic change in colour, which is used as a measure of thermal stability. It should be mentioned that, it is not a measure of absolute thermal stability even though the observed colour changes may be evidence of degradation [16].

In Table 5, according to static heat stability test the colour change (ΔE) of eight PVC composites are presented. At the first time interval (10 min.) except composites containing ZB-ATH (PVC2), individual MH (PVC4) and

ZB-ATH-MH combination (PVC7), other composites provided the same or less colour change compared to plain PVC. But at the progressive time intervals (20 and 30 min.), almost all of flame retardant composites have less colour change than plain composite. This means that, addition of flame retardants improve the heat stability of PVC composites and enhance the resistance to degradation.

3.5 Microstructure by Scanning Electron Microscopy

The cross-section morphologies of PVC composites were observed by SEM and depicted in Figure 6a-d. There are observable pores in the microstructure of PVC0, PVC1 and PVC7. The middle part of micrograph 6c (not the huge porous side) shows the PVC1 composite and, at that part some fine constituents like filler and/or agglomerations of chemicals are present. At given magnifications in Figure 6a-b, no significant difference is observed between plain PVC (PVC0) and PVC containing ZB (PVC1). Additionally, SEM morphology revealed that PVC composites exhibited morphology of same structure (Figure 6a,b,d).

4 Discussion

Adhering to the content of the commercial product, PVC formulations were prepared with fixed amounts of heat stabilizer, impact modifier, wax, pigment and filler. In this research only flame retardant type, amount and combinations were changed, the individual and synergistic effects of flame retardants were studied. Due to the PVC composite content made up of more than 6 different additives, the flame retardancy is a complex subject and usually requires of balancing flammability, heat stability, physical and thermal properties.

When flame retardancy characteristics of PVC composites were examined, it was seen that ZB addition to composite better prevented flammability. ZB-ATH, ZB-MH and ZB-ATH-MH combinations were determined as good alternatives to individual ZB as flame retardants in PVC. Both ZB, ATH and MH contain water of hydration which they release at a temperature below 450°C and dilute the combustible pyrolysis products. In the ZB-ATH synergism, HCl causes to release boric acid from ZB producing B_2O_3 which can form a glassy layer sintering together the Al_2O_3 remaining from ATH dehydration. So, this formed layer inhibit the oxidation of the formed char.

Figure 6: SEM micrographs of PVC0 (a), PVC1 (b,c) and PVC7 (d).

ZB decreased tensile strength of composites, agglomerate formation may be the cause of this result. Synergism of ZB-ATH-MH provided higher tensile strength than ZB-ATH combination. As opposed to the mechanical behaviour, ZB added composites had better elongation at break values. These outcome was valid also for ZB-ATH synergism.

Flame retardants slightly affected Vicat softening temperatures of composites compared to plain PVC. Besides, ZB and ZB-ATH combinations increased softening point. Fusion characteristics as fusion time showed that, ZB-ATH-MH synergism caused quicker gelation. Higher levels of ZB-ATH combination and ZB-MH also reduced fusion time of composites. ATH and MH are economical flame retardants, on the other hand MH has an advantage of better thermal stability. According to heat stability results, almost all of the flame retardants provided less colour change (less degradation) to composites than plain composite. ZB-ATH-MH combination in

PVC improved thermal stability and caused more char residue up to 600°C. This combination increased the thermal degradation temperature and reduced the heat of degradation. Finally, when economical conditions and composite characteristics are considered together, ZB-ATH-MH combination can be recommended as an effective flame retardant to PVC instead of ZB.

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References

- [1] Lyon R.E., In Handbook of Building Materials for Fire Protection, Harper C.A. (Ed.), Chapter 3, McGraw-Hill, 2004.

- [2] O'Mara M.M., Ward W., Knechtges D.P., Meyer R.J., In *Flame Retardant Polymeric Materials*, Kuryla W.C., Papa A.J. (Eds), vol. 1, Marcel Dekker: New York, 1973, 193-273.
- [3] Basfar A.A., Effect of various combinations of flame-retardant fillers on flammability of radiation cross-linked poly(vinyl chloride) (PVC), *Polym. Degrad. Stabil.* 2003, 82, 333-340.
- [4] Hegazy E-S.A., Seguchi T., Machi S., Radiation-induced oxidative degradation of poly(vinyl chloride), *J. Appl. Polym. Sci.*, 1981, 26(9), 2947-2957.
- [5] Jia P., Hu L., Feng G., Bo C., Zhou J., Zhang M., Zhou Y., Design and synthesis of a castor oil based plasticizer containing THEIC and diethyl phosphate groups for the preparation of flame-retardant PVC materials, *RSC Advances*, 2017, 7, 897-903.
- [6] Jia P., Ma Y., Zhang M., Hu L., Li Q., Yang X., Zhou Y., Flexible PVC materials grafted with castor oil derivative containing synergistic flame retardant groups of nitrogen and phosphorus, *Sci. Rep.*, 2019, 9, 1766.
- [7] Zhang Z., Wu W., Zhang M., Qu J., Shi L., Qu H., Xu J., Hydrothermal synthesis of $4\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ /RGO hybrid material and its flame retardant behavior in flexible PVC and magnesium hydroxide composites, *Appl. Surf. Sci.*, 2017, 425, 896-904.
- [8] Qi Y., Wu W., Han L., Qu H., Han X., Wang A., Xu J., Using TG-FTIR and XPS to understand thermal degradation and flame-retardant mechanism of flexible poly(vinyl chloride) filled with metallic ferrites, *J. Therm. Anal. Calorim.*, 2016, 123(2), 1263-1271.
- [9] Levchik S.V., Weil E.D., Overview of the recent literature on flame retardancy and smoke suppression in PVC, *Polym. Adv. Technol.*, 2005, 16, 707-716.
- [10] Qu H., Wu W., Xie J., Xu J., A novel intumescent flame retardant and smoke suppression system for flexible PVC, *Polym. Adv. Technol.*, 2011, 22, 1174-1181.
- [11] Lomakin S.M., Zaikov G. E., *New Concepts in Polymer Science Modern Polymer Flame Retardancy*, Brill Academic: Netherlands, 2003.
- [12] Genovese A., Shanks R.A., Structural and thermal interpretation of the synergy and interactions between the fire retardants magnesium hydroxide and zinc borate, *Polym. Degrad. Stabil.*, 2007, 92(1), 2-13.
- [13] ASTM D2863-13, Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index), ASTM International, West Conshohocken, PA, 2013.
- [14] ISO 1421:2016, Rubber- or plastics-coated fabrics - Determination of tensile strength and elongation at break, International Organization for Standardization, 2016.
- [15] TS EN ISO 306, Plastics - Thermoplastic materials - Determination of Vicat softening temperature (VST), Turkish Standards Institution, Ankara, 2016.
- [16] ASTM D2115-04, Standard Practice for Oven Heat Stability of Poly(Vinyl Chloride) Compositions, ASTM International, West Conshohocken, PA, 2004.
- [17] Kilinc M., Cakal G.O., Bayram G., Eroglu I., Özkaz S., Flame retardancy and mechanical properties of pet-based composites containing phosphorus and boron-based additives, *J. Appl. Polym. Sci.*, 2015, 132(22), 42016.
- [18] Ning Y., Guo S., Flame-Retardant and Smoke-Suppressant Properties of Zinc Borate and Aluminum Trihydrate-Filled Rigid PVC, *J. Appl. Polym. Sci.*, 2000, 77, 3119-3127.
- [19] Gönen M., Balköse D., Ülkü S., Supercritical ethanol drying of zinc borates of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, *J. Supercrit. Fluid.*, 2011, 59, 43-52.
- [20] Elbasuney S., Novel multi-component flame retardant system based on nanoscopic aluminium-trihydroxide (ATH), *Powder Technol.*, 2017, 305, 538-545.
- [21] Al-Ghamdi A.A., El-Tantawy F., New electromagnetic wave shielding effectiveness at microwave frequency of polyvinyl chloride reinforced graphite/copper nanoparticles, *Composites: Part-A*, 2010, 41, 1693-1701.
- [22] Shnawa H.A., Khalaf M.N., Jahani Y., Taobi A.A.H., Efficient thermal stabilization of polyvinyl chloride with tannin-Ca complex as bio-based thermal stabilizer, *Materials Sciences and Applications*, 2015, 6, 360-372.
- [23] Gottschalk A., Breulmann M., Fetter E., Kretschmer K., Bastian M., Application Study: PVC becoming even "hotter", *Kunststoffe International*, 2006/07, 48-50.
- [24] Titow M.W., *PVC Technology*, 4th Edition, Springer Science & Business Media, 2012.
- [25] Comeaux E.J., Chen C.H., Collier J.R., Wesson R.D., Fusion study of polyvinyl chloride (PVC): Relation of processing time and processing temperature to the degree of fusion, *Polymer Bulletin*, 1994, 33(6), 701-708.
- [26] Matuana L.M., Kim J.-W., Fusion characteristics of rigid PVC/wood-flour composites by torque rheometry, *Journal of Vinyl & Additive Technology*, 2007, 13(1), 7-13.