U.P.B. Sci. Bull., Series C, Vol. 71, Iss. 4, 2009 ISSN 1454-234x

INFLUENCE OF THE HALOGEN-FREE ADDITIVES CONCENTRATION ON FIREPROOFED COMPOSITE MATERIALS PROPERTIES

Aurelia IONESCU[1], Petru V. NOŢINGHER[2], Laszlo TARKO[3], Sanda COTESCU[4], Lidia AVĂDANEI[5], Cornel PREDUŢ[6]

Realizarea unor materiale ignifugate cu aditivi fără halogeni reprezintă una din cerinţele importante pentru aplicaţii în multe domenii. În lucrarea de faţă se prezintă o parte din rezultatele obţinute de autori privind realizarea unor materiale compozite ignifugate pe bază de polipropilenă şi poliamidă, cu aditivi fără halogeni.

Se analizează influenţa aditivilor (melamina, teflon) asupra unor proprietăţi fizice (temperatura de topire, indicele de curgere) şi electrice (rezistivitatea, permitivitatea etc.) ale compozitelor realizate şi se arată că influenţa concentratiei de aditivi este mai importantă în cazul rezistivităţii şi mai puţin importantă pentru permitivitate şi pentru factorul de pierderi.

The achievement of the composite materials fireproofed by using halogen-free additives is the one of the important requirements in the applications in many domains. In this paper, we present a part of the results acquired by the autors redarding the obtaining of the fireproofed polypropylene and polyamide based composite materials with halogen-free additives.

We analyse the influence of the additives (melamine, teflon) on the physical (melting point, flow index) and electrical (volume resistivity, relative permittivity and loss factor) properties of the obtained composite materials, and it can notice that the influence of the additives content is more important in case of the resistivity and less important for the permittivity and for the loss factor.

Keywords: polymers, halogen-free additives, fireproofed composite materials

1. Introduction

Owing to their nature, most of the polymer-based materials are combustible. However, the change of their composition and structure by adding of some halogen based additives has enabled the decrease of their susceptibility of burning.

---

[1] Researcher, ICPE S.A. Bucharest , Romania, e-mail: aurionescu@gmail.com
[2] Prof., Electrotechnical Materials Laboratory, University POLITEHNICA of Bucharest, Romania
[3] Researcher, Center of Organic Chemistry - Bucharest - Romanian Academy, Romania
[4] Researcher, ICPE S.A. Bucharest, Romania
[5] Researcher, ICPE S.A. Bucharest, Romania
[6] Researcher, ICPE S.A. Bucharest, Romania

The greatest disadvantage of the composite materials fireproofed by using halogen additives is that, when in contact with fire, they release toxic and corrosive gases. The increasing risk of the use of such fireproofing systems to public health – during production, processing, recycling, and in the stage of waste destruction by incineration - has been distinguished lately [1]-[9].

In a previous paper [10] was presented, in extenso, a method for obtaining of some halogen-free fireproofed composite materials and a part of the tests performed for the study of their flammability. It shows that the use of the melamine and the melamine cyanurate as additives determines an important improvement of the polypropylene and polyamide fire behaviour.

In this paper are presented a part of the experiments conducted with the in view of the characterization, respectively to identify the influence of the halogen-free additives concentration on some physical (melting point, flow index), and electrical (volume resistivity, relative permittivity, loss tangent) properties of this materials. These tests are necessary in order to prepare the microscale production of these materials and their use in different applications.

2. Experiments

2.1. Samples

The tests were performed on two types of composite materials, A and B. The A composite material contains polypropylene homopolymer PP J 600, melamine (AZO MURES SA) and teflon (polytetrafluoroethyelene powder - HOSTAFLON TF-9205, Hoechst-Germany) and the B composite material contains polyamide PA6 (Samid SB, SINDFIBRE S.R.L. Savinesti) and melamine cyanurate (MELAPUR MC 50, CIBA).

The general characteristics of the used component materials are presented in the Table 1 [11]-[13].

Table 1

Characteristics of the component materials

Characteristics	PP J 600	Melamine	Teflon	PA6	Melapur
Melting point (^{0}C)	180.0	-	326	-	-
Flow index	15.4	-	-	-	-
Aspect	-	cristaline powder	-	-	-
Melamine content (%)	-	99.8 ± 0.1	-	-	-
Humidity (%)	-	max. 0.1	-	-	-
Water solution pH at 20 ºC	-	8.5 ± 0.5	-	-	-
Ash content (%)	-	max. 0.01	-	-	-
Medium diameter of particles (μm)	-	-	6 - 9	-	-
Bulk density (kg/dm^3)	-	-	0.3 - 0.5	-	0.15 - 0.20

Specific surface (BET) (m^2/g)	-	-	5	-	-
Density (g/cm^3)	-	-	2.2	-	-
Relative viscosity in H_2SO_4	-	-	-	2.46	-
Tensile stress at break (MPa)	-	-	-	79.53	-
Tensile stress at break (%)	-	-	-	23.21	-
Charpy notched impact (kJ/m^2)	-	-	-	5.1	-

The specimens used for the electrical properties measurements were flat samples with the diameter of 100 ± 0.5mm and the thickness of 3 ± 0.5mm.

2.2. Setups

The fireproofed composite materials were obtained on a pilot setup with a double-screw extruder (L/D = 25 and D = 90 mm), water bath, granulator, vibrator screen and dryer.

For the achievement of the samples, an injection machine of the MI TP 100/50 type (S.C. IMATEX Tg. Mures) with the screw diameter - 35 mm, melting capacity - 96 cm^3, injection pressure - 100-120 MPa, number of heating zones – 4 (three per cylinder and one on the injection die) was used.

For the resistivity measurements a setup including a Keithley 6517A electrometer (10^{-15} A, 1000 V, cc), an 8009 test fixture and a PC with data acquisition programme was used [14] (Fig. 1). The relative permittivity and the loss factor were measured with a RLC bridge Hewlett Packard 263B, and a test fixture Agilent 16451B [14] (Fig. 2).

The melting point was determined by using a Boetius melting point apparatus, and the flow index was determined by using a Melting flow index apparatus .

Volume resistivity was determined (at 100 V and 1 minute) and the relative permittivity ε_r and the loss factor were determined for the frequency values between 1 and 100 kHz.

For each type of material a number of 5 specimens were tested and the mean value was calculated.

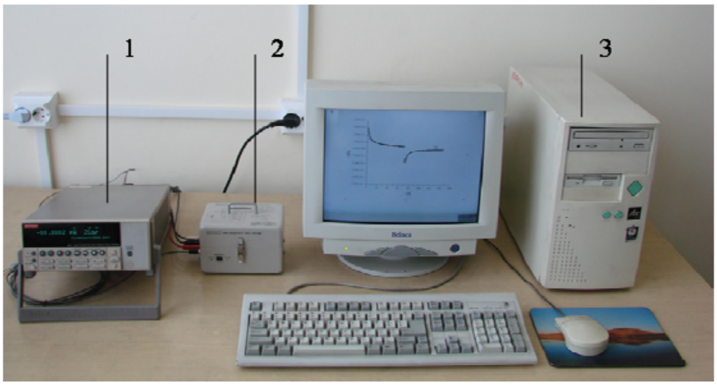

Fig. 1. Resistivity measurement setup: 1 – Keithley 6517, 2 –Keithley 8009 Test Fixture, 3 – PC.

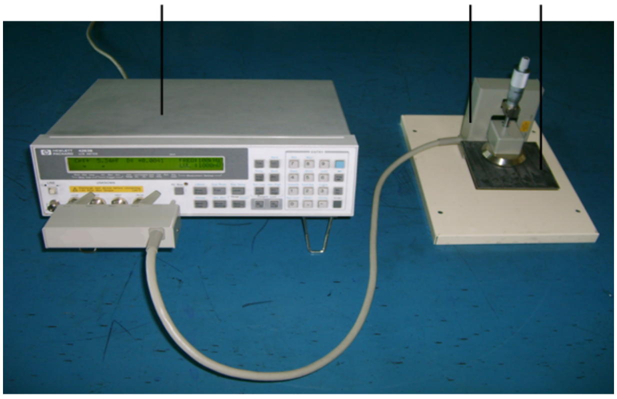

Fig. 2. Relative permittivity and the loss factor measurement setup: 1 –RLC bridge Hewlett Packard 263B; 2 –Agilent 16451B Test Fixture; 3 – Sample.

3. Results and discussions

3.1. Polypropylene based composite materials

For the melting point (T_m) and flow index (I_f) determination a number of 45 samples with different composition (75–100 % polypropylene PP J 600, 0 – 25 % melamine and 0 – 2 % teflon) were tested. Part of the test results are presented in Table 2.

3.1.1. Melting point

The experimental (T_{me}) and the calculated (T_{mc}) values of the melting point are presented in Table 2.

Table 2

Values of the experimental (T_{me}) and calculated (T_{mc}) melting point

Sample	PP J600 (%)	Melamine (%)	Teflon (%)	T_{me} (^{0}C)	T_{mc} (^{0}C)
1	100	0	0	180.0	178.8
2	90	10	0	177.0	179.6
3	85	15	0	179.5	180.0
4	80	20	0	183.0	180.4
5	75	25	0	181.0	180.8
6	74.6	24.9	0.5	179.5	181.3
7	74.25	24.75	1.0	182.0	181.7
8	73.9	24.6	1.5	183.5	182.2
9	73.6	24.4	2	182.0	182.7

It can notice that there is no variation of the values of T_{me} with the melamine (the T_{me} varies between 177 ^{0}C and 183 ^{0}C) and the teflon (the T_{me} varies between 179.5 ^{0}C and 183.5 ^{0}C) contents.

On the other hand, the obtained results have fuzzy values and it cannot be drawn a clear conclusion regarding the influence of the melamine and the teflon content on the melting point [15].

The linear correlation between the melting point and the melamine content P_{mel} is small (r^2 = 0.2984), and the linear correlation between the melting point and the teflon content P_{tef} is small too (r^2 = 0.2952), where r^2 is the square linear Pearson correlation having values in the interval of [0, 1].

The application of the Least Square Method leads to the equation:

$$T_{mc} = 178.7611 + 0.0829\ P_{mel} + 0.9345\ P_{tef}, \quad (1)$$

where P_{mel} is the melamine content, and P_{tef} is the Teflon content.

The linear correlation between the calculated values and the measured values of the melting point (Table 2) is very small (r^2 = 0.3803; F = 2.15), where F is the Fisher function, having values in the interval [0, ∞] and the equation $F = \frac{r^2}{1-r^2} * \frac{(N-p)}{p}$, where N is the number of the cases in the calibration set, r^2 is the square linear Pearson correlation and p is the number of the descriptors in the equation used for the prediction.

3.1.2. Flow index

The experimental (I_{fe}) and the calculated (I_{fc}) values of the flow index are presented in Table 3.

Table 3

Values of the experimental (I_{fe}) and calculated (I_{fc}) flow index

Sample	PP J600 (%)	Melamine (%)	Teflon (%)	I_{fe}	I_{fc}
1	100	0	0	15.4	14.1
2	90	10	0	14.7	15.3
3	85	15	0	14.8	15.8
4	80	20	0	13.3	16.4
5	75	25	0	19.8	17.0
6	74.6	24.9	0.5	15.6	14.8
7	74.25	24.75	1	12.9	12.6
8	73.9	24.6	1.5	9.9	10.4
9	73.6	24.4	2	8.3	8.2

Not even for the flow index can one ascertain a valid influence of the melamine content (I_{fe} varies between 13.321 and 19.785). On the other hand, the values of I_{fe} decrease from 15.619 to 8.318 when the teflon content increase from 0 to 2 %.

The linear correlation between the flow index and the melamine content P_{mel} is very small (r^2 = 0.0516), but the linear correlation between the flow index and the teflon content P_{tef} is large (r^2 = 0.6927).

The application of the least square method leads to the equation:

$I_{fc} = 14.0682 + 0.1185\, P_{mel} - 4.3706\, P_{tef}$. (2)

There is an acceptable linear correlation between the calculated I_{fc} and the experimental I_{fe} values of the flow index ($r^2 = 0.7616$; $F = 11.18$).

3.2. Polyamide 6 based composite materials (PA6)

For the polyamide based composite materials, the volume resistivity (ρ_v), relative permittivity (ε_r) and loss factor (tgδ) have measured using samples with different contents of melapur MC50.

3.2.1. Volume resistivity

The experimental (ρ_{ve}) and calculated values (ρ_{vc}**)** of the volume resistivity (ρ_v**)** are presented in Figure 3 and Table 4.

It can see that the values of ρ_{ve} decrease with the increase of the Melapur content (from 3.88x10^{13} to 0.35x10^{13} Ωm). That is probably due to a bigger conductivity of the Melapur and to a change of the composite material structure.

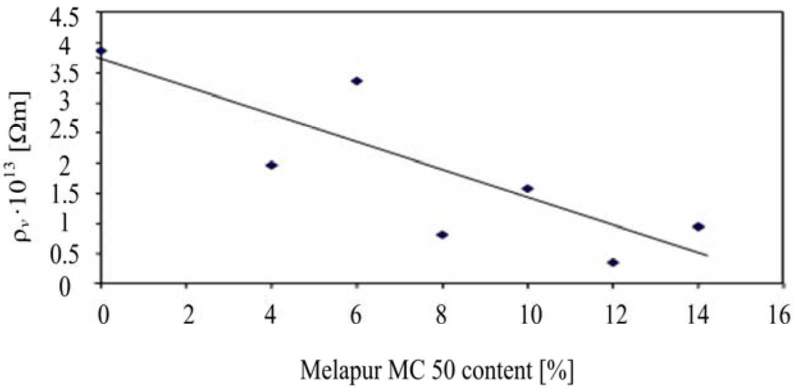

Fig. 3. Dependence of the volume resistivity ρ_{ve} on the Melapur MC50 content.

Table 4

Experimental (ρ_{ve}) and calculated (ρ_{vc}) values of the volume resistivity for PA 6 with different concentrations of MC 50

Sample	Melapur MC50 (%)	$10^{13}\rho_{ve}$ (Ωm)	$10^{13}\rho_{vc}$ (Ωm)
1	0	3.88	3.53
2	4	1.95	2.34
3	6	3.36	3.14
4	8	0.83	1.16
5	10	1.57	1.96
6	12	0.35	0.02
7	14	0.94	0.77

The dependence of the volume resistivity ρ_{vc} on the Melapur content P_{mel}, is done by the equation :

$$10^{13}\rho_{vc} = 4.22 - 0.296P_{mel} + 0.693\cos[90(P_{mel} - 2)]. \quad (3)$$

The linear correlation between the calculated (ρ_{vc}) and the measured values (ρ_{ve}) of the volume resistivity (Table 4) is very large (r^2 = 0.9293; F = 32.86).

3.2.2. Relative permittivity

The experimental (ε_{re}) and the calculated (ε_{rc}) values of the relative permittivity (ε_r) are presented in Table 5 and Figure 4.

Table 5

Values of the experimental (ε_{re}) and calculated (ε_{rc}) relative permittivity for PA 6 with different values of the Melapur MC50 content (f = 100 kHz)

Sample	Melapur MC50 (%)	ε_{re}	ε_{rc}
1	0	2.56	2.61
2	4	2.68	2.62
3	6	2.45	2.43
4	8	2.51	2.62
5	10	2.50	2.43
6	12	2.61	2.62
7	14	2.40	2.43

It can see that the values of ε_{re} decrease from 2.56 to 2.40 with the increase of the Melapur MC50 content from 0 to 14 %. That is probably due to a smaller permittivity of the MC50 and a change of the material structure.

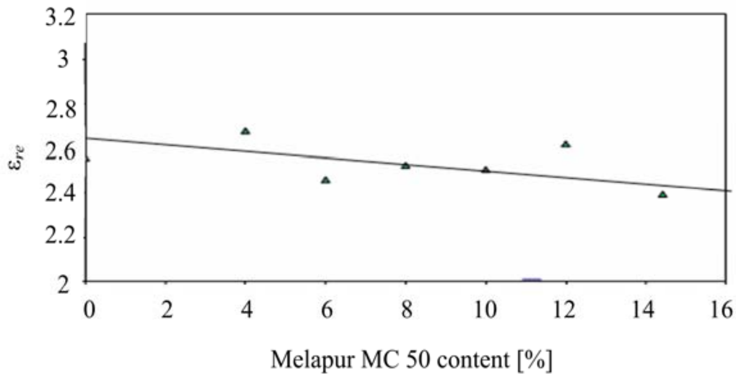

Fig. 4. Dependence of the experimental relative permittivity for PA6 ε_{re} on the Melapur MC50 content (f = 100 kHz)

A dependence of the relative permittivity on the Melapur MC50 content P_{mel}, can be obtained from equation :

$$\varepsilon_{rc} = 2.84 + 0.0003P_{mel} - 0.093\cos[90(P_{mel} - 2)]. \quad (4)$$

The linear correlation between the calculated (ε_{rc}) and the measured (ε_{re}) values of the relative permittivity is large (r^2 = 0.8378; F = 30.99).

3.2.3. Loss factor

The experimental ($tg\delta_e$) and the calculated ($tg\delta_c$) values of the loss factor are presented in Table 6 and Figure 5.

It can seen that the values of $tg\delta_e$ decrease from $2.75*10^{-2}$ to $2.17*10^{-2}$ with the increase of the Melapur MC50 content from 0 to 14 %.

Table 6

Values of the loss factor of PA 6 for different values of the Melapur MC50 content (f = 100 kHz)

Sample	Melapur MC50 (%)	$10^{-2}. tg\delta_e$	$10^{-2}. tg\delta_c$
1	0	2.75	3.13
2	4	3.25	3.26
3	6	2.62	2.44
4	8	3.55	3.39
5	10	2.74	2.57
6	12	3.51	3.53
7	14	2.17	2.70

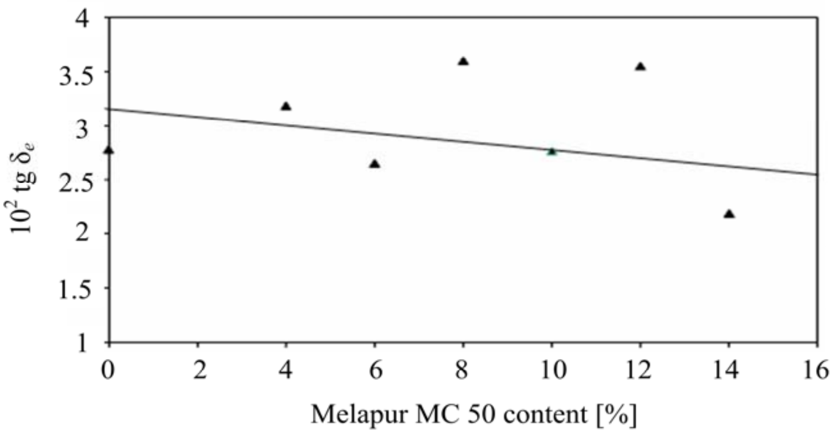

Fig. 5. Dependence of the loss factor $tg\delta_e$ of PA 6 on the Melapur MC50 content (f = 100 kHz).

The dependence of the loss factor $tg\delta$ on the Melapur MC50 content P_{mel} is done by the equation:

$$0.01tg\delta_c = 2.058 + 0.033P_{mel} - 0.447\cos[90(P_{mel} - 2)]. \quad (5)$$

The linear correlation between the calculated and the measured values of the loss factor is medium (r^2 = 0.6978; F = 13.85).

The use of the melamine and the melamine cyanurate as additives determines an important improvement of the polypropylene and polyamide fire behaviour [10].

It can see that the influence of the melamine and the teflon concentration on the melting point of the polypropylene based composite materials is insignificant. On the other hand, the influence of the melamine concentration on the flow index is insignificant too, but the influence of the teflon concentration on the flow index is important.

The values of Melapur MC50 content and the values of the electrical properties presented in the Table 4, 5 and 6 suggest an unlinear dependence, with (co)sinusoidal aspect, of this characteristics on the Melapur MC50 content in the polyamide based composite materials.

Using the equations 1, 2, 3, 4 and 5 it can calculate the values of the studied characteristics (T_m, I_f, ε_r, ρ_v and tgδ) for values of the additive content that are not experimentally obtained.

In Table 7 the values of the polyamide PA 6 halogen – free fireproofed and PA 6 halogen fireproofed electrical properties (measured after 88 hours, at 23^{o}C and 50 % relative humidity) are presented [16]. It can see that the volume and the surface resistivity values are bigger, and the loss factor values are smaller for the first material than for the second.

Table 7

Values of the electrical properties of PA 6 halogen-free fireproofed and of PA 6 halogen fireproofed

Property	Test method	PA 6 halogen-free fireproofed	PA 6 halogen fireprofed
Volume resistivity, ρ_v (Ωm)	CEI 60093-1980	10^{+13}	10^{+12}
Surface resistivity, ρ_s (Ω)	CEI 60093-1980	10^{+11}	10^{+10}
Relative permittivity, ε_r	CEI 60250-1969	2-2,5	2
Loss factor, tg δ	CEI 60250-1969	0,007-0,01	0,01
Electrical strength, E_{str} (kV/mm)	SR EN 60243/1-2000	14	20

From this point of view, it can see that the new product behavior is better than the product with halogen.

Certainly, it must remark that the electrical strength is reduced, but it is elevated sufficient for medium-voltage applications.

4. Conclusions

The melting point and the flow index of the polypropylene based composite material do not practically change for a melamine content of 24,9 % and for a teflon content of 0,5%.

The volume resistivity of the polyamide 6 based composite materials decreases by a magnitude order while the relative permittivity and the loss factor decrease (below 20 %) when the Melapur MC50 content increases.

Consequently, the use of an additive content smaller than 14 % is recommended for the fireproofed composite material achievement.

The essential electrical properties of the halogen-free composite materials are better than those of the halogen composites.

REFERENCES

[1] *C. G. Bienfait*, e.a., Biotechnologie industrielle et chimie durable, 2003 (www.kbr.be)

[2] *** Halogen-free flame-resistant ULTRAMID grades, The Environmentally Acceptable Alternative –BASF Germany, 2003

[3] *Dr. Ottmar Schacker*, Compounding with Ammonium Polyphosphate-Based Flame Retardants, Plastics Additives & Compounding, pg. 28-30, 2002

[4] *Edward A. Myszak, Michael T. Sobus*, Flame Retardant Developments for Polypropylene, Nyacol Nano Technologies, Inc., 2003

[5] *B.W. Moody*, Performance Characteristics of Non-Halogenated\flame Retardant Polypropylene, Proceedings of the SPE 49th Annual Technical Conference, 2001

[6] *** Flame Retardants: Some New Developments, Plastics Additives & Compounding, 2001

[7] *** Halogen-Free Fire Retardancy: Overview and New Approaches, Plastics Additives & Compounding, Mar., 2001

[8] *** Flame Retardants: Some New Developments, Plastics Additives & Compounding, May, pp. 24-27, 2000

[9] *** Halogen-Free Compounds Continue Growth in Wire and Cable, Plastics Additives & Compounding, pp. 36-37, 1999

[10] *Lidia Avadanei*, Method for Production of the Non-Halogen Fireproof Polyamide 6, 3rd European Weathering Symposium, Cracov, Poland, 2007

[11] www.ciba.com

[12] *** Hostaflon Information nr.23, Oct. 1994

[13] www.sablari.lx.ro STR 10911/1982

[14] www.keithley.com

[15] *J. Colven, P. Colven, S.G. Wert, L.S. Aiken*, Applied Multiple Regression/Correlation Analysis for the Behavioural Sciences (3rd ed.), Hillsdale, 2003

[16] http://www.acquistem.ro/pdf/NONHALO.pdf.