COST Action TU1301
NORM for Building materials (NORM4BUILDING)

Short Term Scientific Mission Report

‘Investigation of the possibilities for application of NORM into polymer materials’

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COST-STSM- TU1301-190316-072440

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STSM Grantee	Investigation of the possibilities for application of NORM into polymer materials, Vineta Srebrenkoska				
Home Institution	University Goce Delcev in Stip, Faculty of Technology, Krste Misirkov 10-A, 2000 Stip, Republic of Macedonia				
Host Institution	Slovenian National Building and Civil Engineering Institute, Dimiceva 12, 1000 Ljubljana, Slovenia				
STSM Start Date	19/03/2016	**End Date**	29/03/2016	**Duration**	11 days

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1. Purpose of the STSM

This STSM is closely linked to the aims of working group 2 in the frame of the COST Action TU1301 and strongly supports the WG 2 activity and directly enables the development of new options for tailor-made polymer composite material for building which incorporates NORM. The fundamental structure of the STSM is based on characterizing of the thermoplastic and thermoset polymer materials and fly ashes in accordance with the final application in polymer composite materials based on NORM.

The purpose of the stay was focused on the realization of the analyses of the inorganic fillers and organic polymer matrices and it was made with the following aim:

- to find the most effective filler strengthening configuration,
- to quantify the thermomechanical characteristics of the thermoset and thermoplastic polymers,
- to better understand the interaction between fillers and a matrix,
- to estimate the contribution of the fillers, matrix and designed composite systems for the thermomechanical properties,

The desired objectives of the STSM were achieved by the strong co-operation between Slovenian National Building and Civil Engineering Institute (ZAG) and Goce Delcev University in Stip, using the complementary competences of both research groups.

2. Description of the work carried out during the STSM

The focus of this stay was thermal testing of the different epoxy resins as a thermoset polymer materials and PPS (polyphenylene sulphide) as a thermoplastic polymer by TGA and DSC. Also characterization of the fly ash from Slovenia, type V-333/14 (chemical composition and distribution of the particle size) was performed.

The different models of polymer composites based on fly ash were performed. For the production of the composites the epoxy resin system TW100/TW120 from Hustman and fly ash from Slovenia were used. First the epoxy resin system was performed by using 100 parts by weight from epoxy TW100 and 22 parts by weight from epoxy TW120. Then, the different amount of fly ash was impregnated into the epoxy resin system by mixing. The preparation of the composites was done by applying the mechanical stirrer at the room temperature (Figure 1). The illustration of the resin system, fly ash and mixture systems epoxy/fly ash are presented at figure 2. Three test specimen configurations were made: one from the epoxy resin system and two with different content of fly ash (Table 1).

Table 1. Test specimens configuration

Sample designation	Sample description	Content of fly ash, % by weight
1	Epoxy resin system TW100/TW120	0
2	Epoxy resin system/fly ash	30
3	Epoxy resin system/fly ash	50

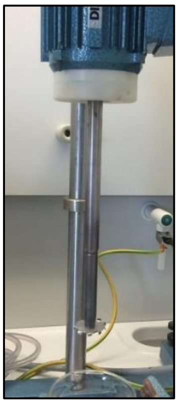


Figure 1. Illustration of the mechanical stirrer

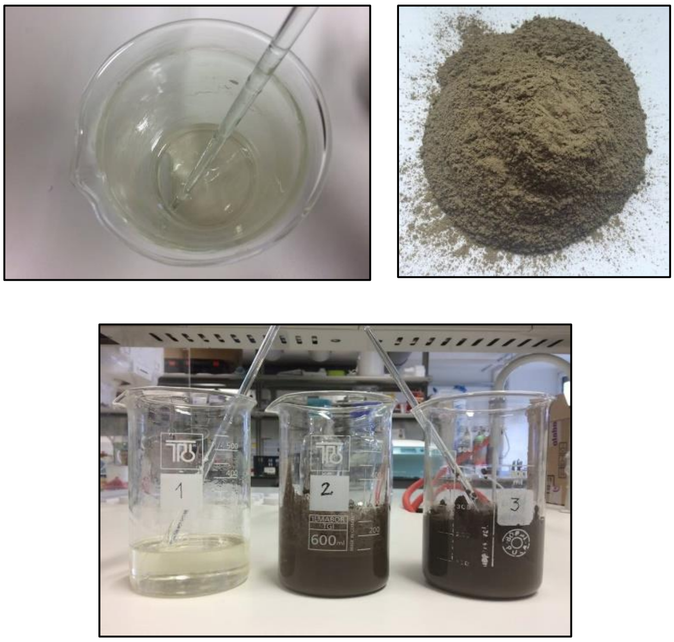


Figure 2. Illustration of the epoxy resin system, fly ash and mixture systems epoxy/fly ash

Samples with different content of fly ash as well as the samples from epoxy resin system were put into the mold (Fig. 3) according the ISO 178 standard for mechanical testing and then cured with industrial heater at 70°C, for four hours.

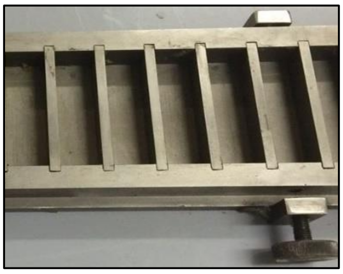


Figure 3. Specimens mold

The chemical composition of the fly ash from Slovenia was performed with ARL PERFORM'X Sequential XRF instrument (Fig. 4) and also a particle size distribution was determined.

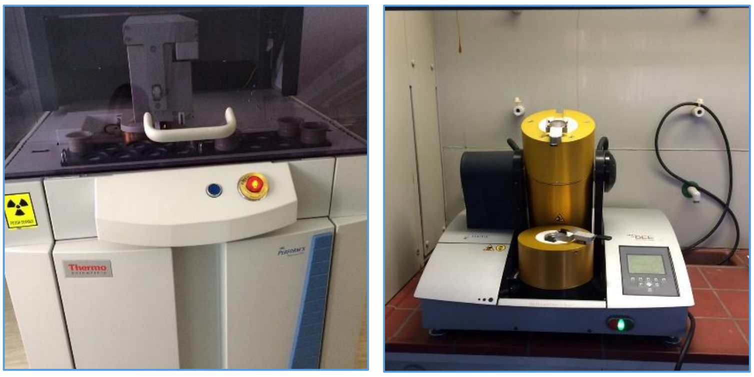


Figure 4. ARL PERFORM'X Sequential XRF instrument

The focus of work carried out during the STSM was the thermal characterization of the epoxy resin system (uncured and cured) and composites with different content of fly ash by using of Thermal Gravimetry- TG and Differential Thermal Analyses - DTA methods as well as mechanical characterization of the PCMs with fly ash.
The TG/DTA/DSC measurements were performed with a NETZSCH instrument: STA 409 PC/PG . The experiments were carried out under a constant flow of AIR (80/20)/10/AIR (80/20)/20. About 6 mg of each sample was heated from 20 ^{o}C to 600 ^{o}C at a heating rate of 10 K/min (Fig.5).

Figure 5. TG/DTA NETZSCH instrument

For the determination of the flexural properties from each configuration five test specimens were prepared according to ISO 178 standard (Fig. 6). Flexural tests of 17 samples were carried out at room temperature using universal testing machine Zwick Z-100 with loading speed of 10 mm/min (Fig. 7).

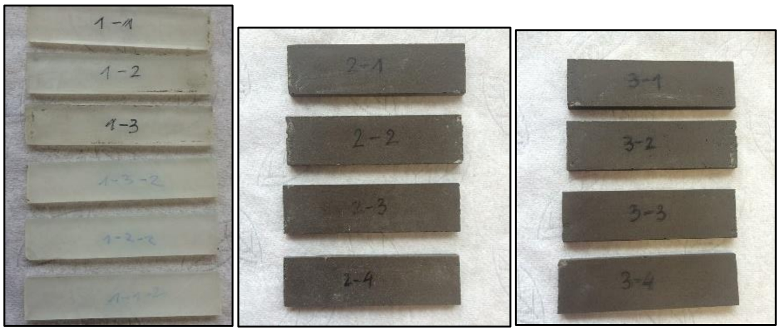


Figure 6. Illustration of the test specimens for flexural testing

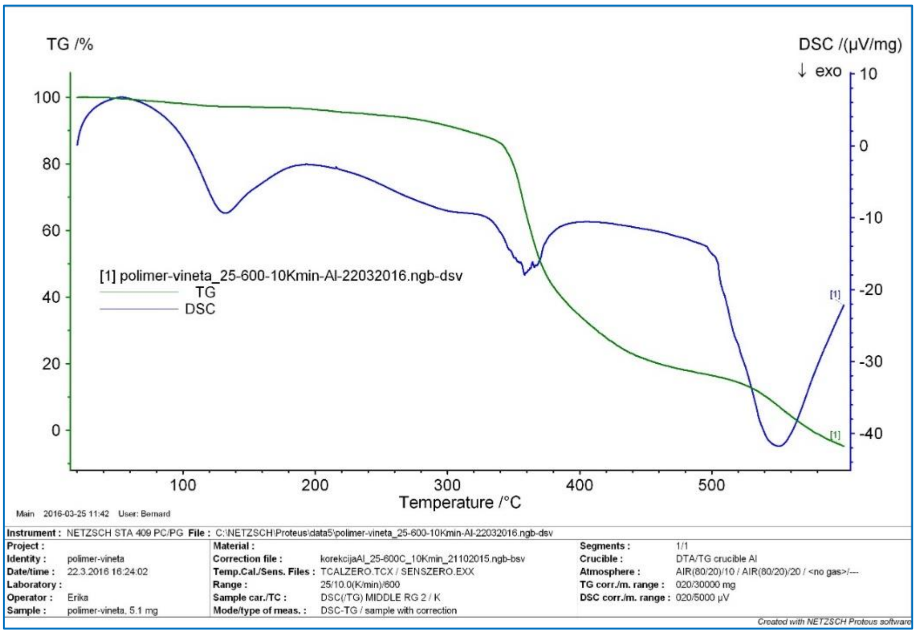
Figure 7. Universal testing machine ZWICK Z-100

3. Description of the main results obtained

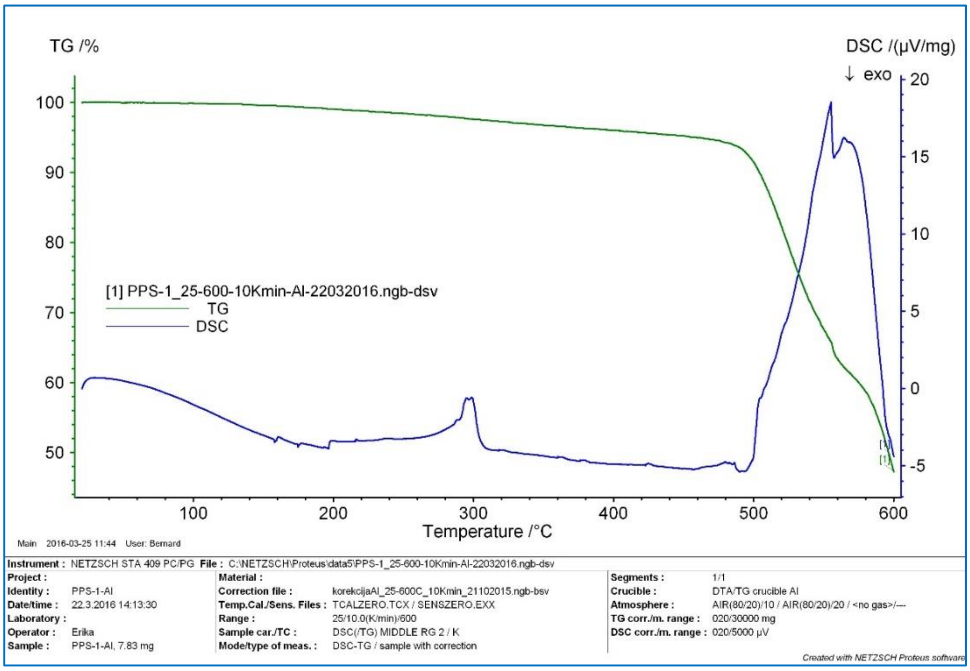
The thermal characteristics of the epoxy resin system (uncured and cured) and PPS and of the different models of epoxy/fly ash composites were measured using both Differential Thermal Analyses (DTA) and Thermo Gravimetric (TG) methods.

The thermal measurements of the polymer materials (thermoplastic and thermoset) and polymer composites with NORM are useful in determining the key physical and chemical characteristics of the resin and of the composites, including: glass transition or softening temperature (Tg), onset and completion of cure, heat of cure, maximum rate of cure, percent cure, heat capacities (Cp). These properties can be used to address some of the problems: establishment of optimal processing conditions, estimation of percent cure of end products, analyses of competitive materials etc.

The results from the thermogravimetric analyses of an uncured epoxy resin system and PPS are presented in Figure 8.



a) TG/DSC for uncured epoxy resin system TW100/TW120



a) TG/DSC for uncured PPS

Figure 8. Thermogravimetric curves of an uncured epoxy resin system and PPS: weight loss (%) versus temperature and DSC results

An uncured epoxy resin system loses about 10% of its weight until 350 ^{o}C, followed by ongoing 90% weight loss to 450–500 ^{o}C. After that, the weight loss continues with a slower degradation rate. It should be noted that at a temperature of 600 ^{o}C, the epoxy resin system exhibit residual weight of about 8%. The thermoplastic polymer PPS loses about 8% of its weight until 500 ^{o}C and after that from 500 – 600 ^{o}C it loses the rest of 90% of its weight.

Polyphenylene sulfide (PPS) is an engineering plastic, commonly used today as a high-performance thermoplastic. PPS can be molded, extruded, or machined to high tolerances. In its pure solid form, it may be opaque white to light tan in color. Maximum service temperature is 218 °C. PPS has not been found to dissolve in any solvent at temperatures below approximately 200 °C.

From the DSC results the graphs show the heat flow as a function of the sample temperature. The glass temperature event (Tg) is observed as a stepwise increase in the heat flow or heat capacity. The onset of the cure is the temperature at which the heat flow deviates from the linear response and the peak temperature reflects the maximum rate of curing of the resin. At the completion of curing or crosslinking, the DSC heat flow returns to a quasilinear response. The area of the peak can be integrated to give the heat of cure, ΔHcure (J/g).

As a thermosetting resin cures or crosslinks, two main things happen: Tg increases and heat of cure decreases. Based on the DSC scans for an uncured epoxy resin system, it can be noticed that, two exothermic peaks were observed at heating rate 10 K/min. In the first peak the glass transition temperature (Tg) is observed at a temperature of about 103°C, whereas in the second peak glass transition temperature (Tg) has been increased to 280°C. Based on the DSC scans for thermoplastic polymer PPS, it can be noticed that the glass transition temperature (Tg) is at a temperature of about 110°C, whereas the melting temperature (Tm) is at about 300°C.

The results from the TG/DSC analyses of cured epoxy resin system at 70^{0}C for 4h are presented in Figure 9.

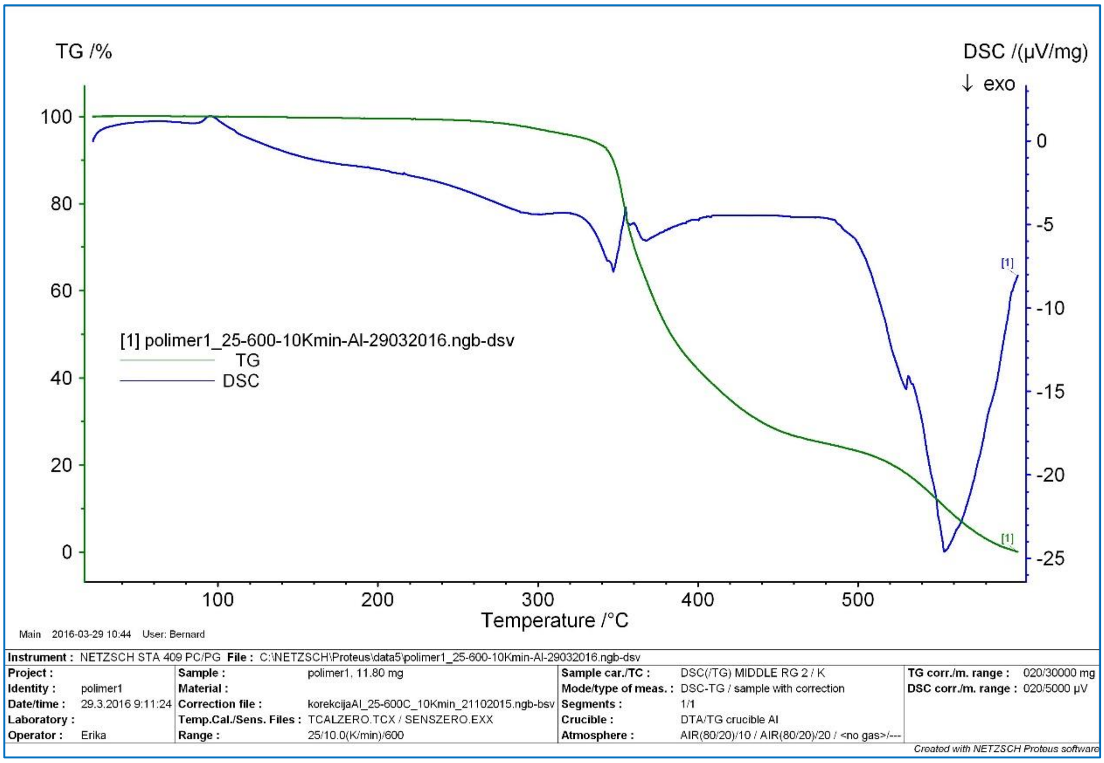


Figure 9. TG/DSC for cured epoxy resin system TW100/TW120

A cured epoxy resin system loses about 10% of its weight until 350 ^{o}C, followed by ongoing 80% weight loss to 450–500 ^{o}C. After that, the weight loss continues with a slower degradation rate.

The chemical composition of the fly ash from Slovenia are presented in the table 2 and the particle size distribution in the table 3.

Table 2. Chemical composition of the Slovenian fly ash V-333/14

Component	Content in fly ash V-333/14, %
SiO_2	39,64
Al_2O_3	17,34
Fe_2O_3	7,23
MgO	4,35
CaO	17,48
Na_2O	0
K_2O	1,63
TiO_2	0,51
LOI	5,01
P_2O_5	0,96

Table 3. Particle size distribution

Particle diameter (μm)	V333/14, % mas.
0,1	0,69
0,4	2,08
0,9	2,80
1	2,88
2	4,05
6	11,33
10	18,56
12	21,49
18	28,55
20	30,61
30	39,59
40	46,52
63	58,59
90	69,39
100	72,36
125	77,84
200	85,05
250	87,91
400	95,01
500	97,10
1000	99,31
2000	99,98
4000	100,00
8000	100,00

The testing metod results of the test specimens for determination of the flexural strength of the cured epoxy resin system are presented in Figure 10 and Table 4.

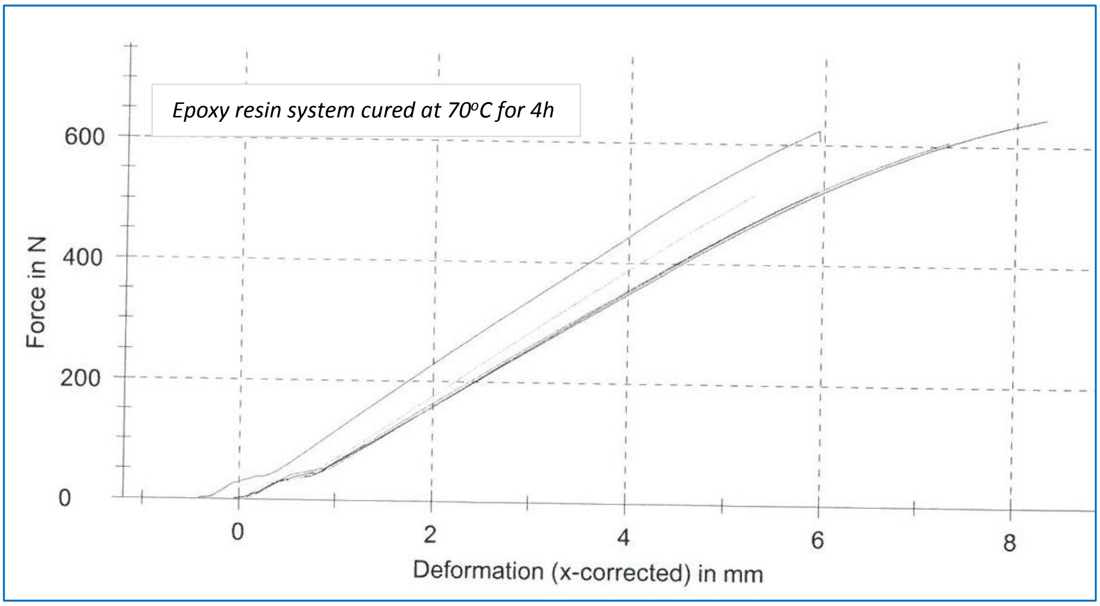
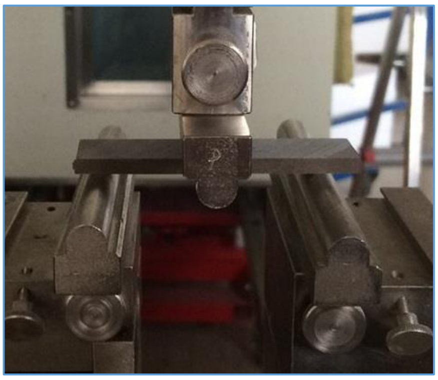


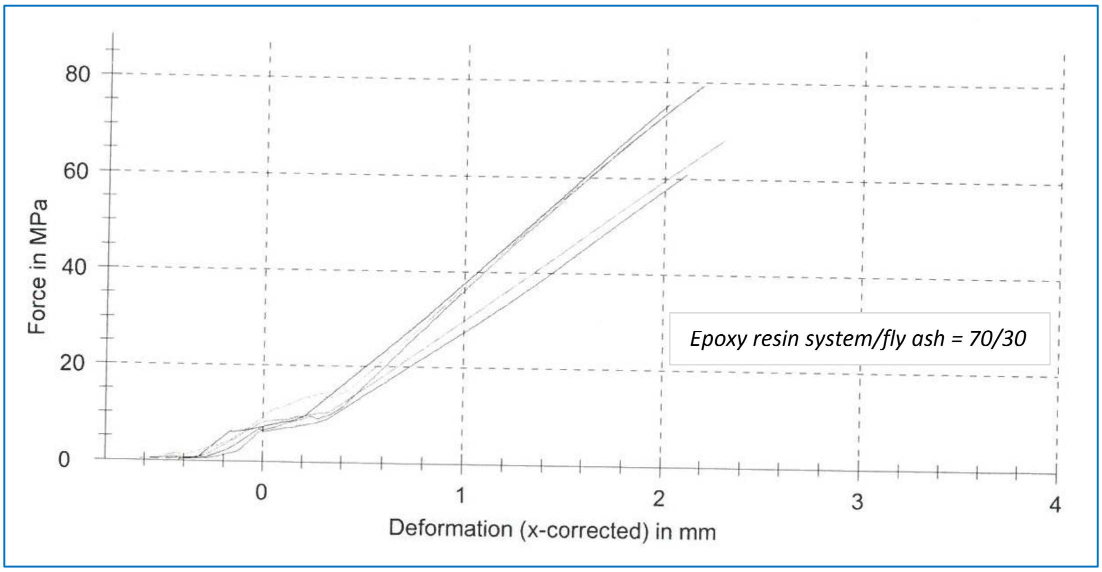
Figure 10. Force and displacement curves of epoxy resin system samples – **series 1** from Zwick Z 100 universal tensile testing machine

Table 4. Results of the flexural strength of the epoxy resin system cured at 70°C for 4h

Designation of the samples	**E_f, MPa**	**σ, MPa**	**ε, mm**	**ε, %**
1 -1	3750	139	5,95	4,1
1-2	2380	144	7,30	4,8
1-3	2500	153	8,30	5,5
1-4	2940	119	5,31	3,6
1-5	2200	120	5,96	4,0
Statistics Series n = 5				
$\bar{x}$	2750	135	6,75	4,4
s	621	15,0	1,21	0,8
ν	22,55	11,09	18,47	17,40

Figures 11 shows a typical force and displacement curves at ambient temperature for tested samples series 2 and 3 and the results of the flexural strength of polymer composite material with NORM are presented in Table 5 and 6.





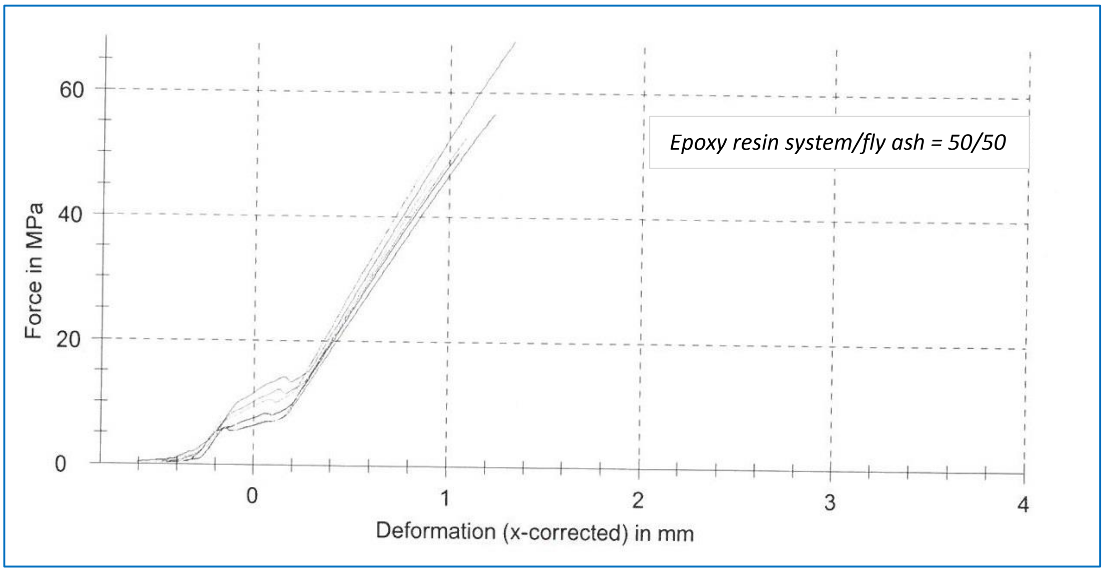


Figure 11. Force and displacement curves of composites: epoxy resin system/fly ash, samples – **series 2** and **series 3** from Zwick - 100 universal tensile testing machine

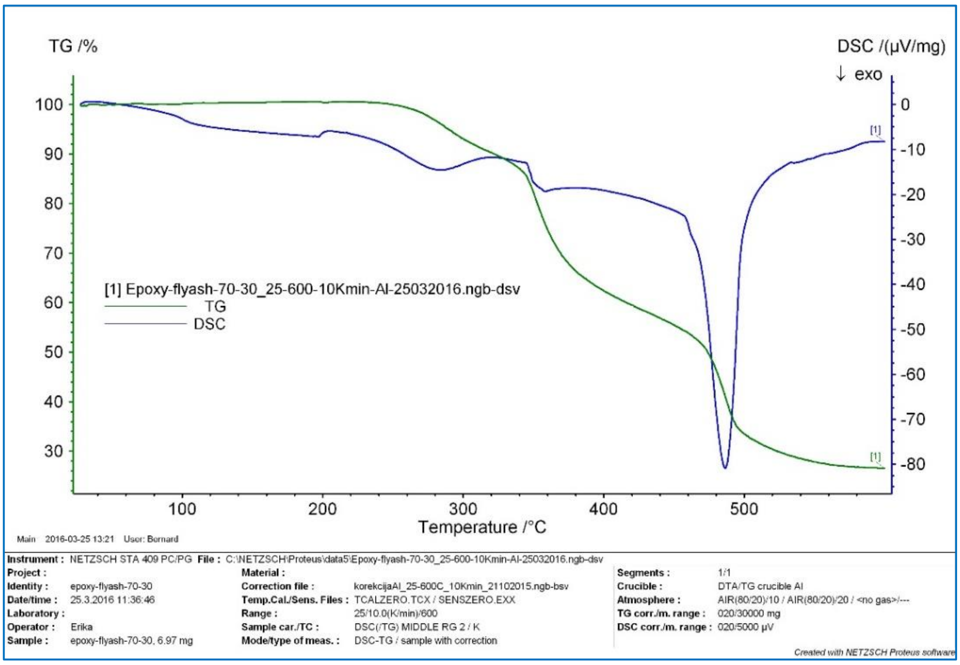
Table 5. Results of the flexural strength of the PCMs with fly ash: epoxy resin system/fly ash = 70/30 %wt.

Designation of the samples	E_f, MPa	σ, MPa	ε, mm	ε, %
2 -1	4060	60,9	2,11	1.4
2-2	4310	68,2	2,30	1,6
2-3	5460	75,4	2,02	1,4
2-4	5400	79,5	2,20	1,5
2-5	5490	79,2	2,18	1,5
Statistics: Series n = 5				
$\bar{x}$	4940	72,6	2,16	1,5
s	698	8,01	0,11	0,1
v	14,12	11,02	4,91	5,23

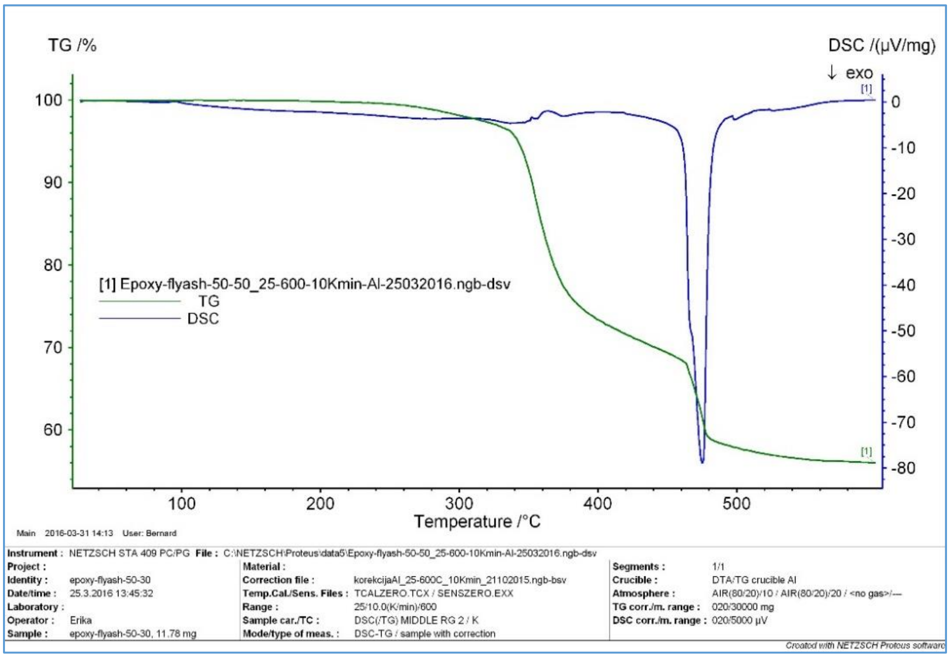
Table 6. Results of the flexural strength of the PCMs with fly ash: epoxy resin system/fly ash = 50/50 %wt.

Designation of the samples	E_f, MPa	σ, MPa	ε, mm	ε, %
3 -1	6920	56,6	1,23	0,8
3-2	7240	52,7	1,09	0,8
3-3	7120	50,2	1,05	0,7
3-4	8250	50,6	0,94	0,6
3-5	7780	68,3	1,33	0,9
3-6	7530	46,3	0,91	0,6
3-7	8170	48,0	0,87	0,6
Statistics: series n = 7				
$\bar{x}$	7570	53,2	1,06	0,7
s	516	7,41	0,17	0,1
v	6,81	13,92	16,27	16,24

The thermal characterization of the PCMs with fly ash, samples – series 2 and series 3 are presented on figure 12.



TG/DSC curves – **series 2**



TG/DSC curves – **series 3**

Figure 12. TG/DSC curves for PCMs with fly ash, samples – series 2 and 3

These investigations in the frame of this STSM stay in the Slovenian National Building and Civil Engineering Institute - ZAG represent a beginning of the future research for possibilities of using the NORM into the polymer materials. Both institution will continue separately with the next investigations for the realization of the established aims. The whole results will be exchanged through a strong collaboration between Slovenian National Building and Civil Engineering Institute (ZAG) and Goce Delcev University in Stip.

4. Future collaboration with the host institution

Preliminary conversation was carried out for the future cooperation in the frame of some European projects like EUREKA, NATO Science for Peace programme etc. The future collaboration will be in the direction of the continuing the investigation connected with the application of the NORM material into polymer matrix.

5. Foreseen publications resulting or to result from the STSM

The results obtained during this STSM stay and also with the ones previously obtained will be presented in a form of mutual publications in well-known international journals. Also, the results of this stay will be presented at several congresses and conferences all over the world and other national conferences.

6. Confirmation by the host institution of the successful execution of the STSM

Please, see confirmation letter in the attached file.

7. Other comments

I would like to express my gratitude to the COST Action TU 1301 for the financial support of this STSM and giving me the chance to make the predicted investigation mainly connected with WG2 activities.

Also, I am grateful to Dr Vilma Ducman and Dr. Andrijana Sever Škapin for hosting me at the Department of Materials /Laboratory for polymers at Slovenian National Building and Civil Engineering Institute - ZAG in Ljubljana, Slovenia and for their exceptional engagement in the course of my involving in preparation of the polymer composites based on NORM, mechanical and thermal measurements, interpretation of the results and theoretical background. Also, many thanks to Dr. Erika Švara Fabjan for her technical help in the thermal measurements during this stay and many thanks to the all from the Institute for polymers for their technical help in the mechanical measurements.

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