UDC 621.311.22:504.5
UDC 66.017

FLY ASH-POLYMER COMPOSITES BASED ON POLYVINYLCHLORIDE AND INDUSTRIAL FLY ASH WASTE PARTICLES

Raman Aliti, Goran Načevski, Gordana Ruseska, Perica Paunović, Anita Grozdanov*

Faculty of Technology and Metallurgy, Univeristy Ss Cyril and Methodius in Skopje,
Rugjer Boskovic 16, 1000 Skopje, R. Macedonia
(anita@tmf.ukim.edu.mk)

Abstract

An alternative filler based on industrial waste particles of Fly Ash (FA) in Poly Vinyl Chloride (PVC) composites was tested in this work. Plasticized PVC was used as a matrix. FA/PVC composite samples were prepared using two different types of FA (FA waste particles obtained as a byproduct from the ferro-nickel production process and FA particles from the coal power plant). The obtained FA particles were chemically modified and used in PVC polymer matrix in order to obtain landfill geomembranes. The FA surface was modified by NaOH and HCl treatment. Concentration of the fly ash was varied in the range of 5, 10 and 20 %. The obtained samples were analyzed by TGA/DTA, FTIR, SEM and swelling test. Uniform reinforcement dispersion in the polymer matrix is very important in order to ensure that there was a good interaction between both constituents that will result in good composite's properties. The microstructural properties of the obtained FA/PVC composites studied by SEM, confirmed region of well dispersed FA particles where fly ash particles were mechanically interlocked in the PVC matrix with good interfacial interaction with the matrix. However, particle agglomeration and voids were observed in composites reinforced with higher amounts of fly ash. Thermal parameters of the PVC composites decreased in the presence of both types of FA. Lower values were obtained due to the HCL treatment of FA particles compared to NaOH treated FA. Generally, all the FA/PVC composites have shown higher swelling degree than PVC.

Key words: *Fly Ash, Polymer Composites, Industrial waste*

Introduction

Besides the fiber-reinforced polymer composites, the particulate composites have received considerable interest in the field of materials because of their potential for large gains in mechanical and morphological properties as well as from the ecological point of view. Thermoplastic polymers and especially Poly Vinyl Chloride (PVC) nowadays are produced and used in huge quantities. They are seldom used as pure polymers and they are usually combined with mineral fillers like fly ash, graphite etc. Fillers find almost exclusively application in the polymer industry to improve mechanical, thermal, electrical properties and dimensional-stability.

Fly ash is a pouzzollanic material, mainly generated as a byproduct or wastes from coal-burning thermal powerplants as well as from the mine production process, and collected by an electrostatic precipitators or a fabric filters (baghouses). Though a significant fraction of coal fly ash is used as a cement and concrete additive in the world, only a very small portion of the million tons of generated fly ash is re-utilized [1-4]. Usually, the FA is disposed of in the form of a slurry in the vicinity of the power plant and fly ash exhibits significant risk into the environment [2,3]. Namely, Fly ash contains a range of heavy metals of different mobility in its structure [2]. Fly ash consist mostly of SiO_2, Al_2O_3, and with Fe_2O_3 they are present in inorganic incombustible matters present in the coal, but depending upon the source of coal, contains elements like carbon, Co, Cr, Ti, Mg, also. So the fly ash possesses combination of properties of spherical particles and that of metals and metal oxides. Due to the increased environmental concern, last decades an intensive work was made to design a wide range of alternative applications that will include the FA waste particles [5-8].

The effect of FA on different properties of polymer composites has been studied by a number of researchers. Deepthi *et al.* were studied the mechanical and thermal characteristics of High Density Poly-ethylene— fly ash cenospheres composites [6]. Fujino and Honda have explored the measurement of the specific heat of plastic waste fly ash composite material using differential scanning calorimetry [9]. The effect of fly ash on the mechanical, thermal, dielectric, rheological and topological properties of filled nylon 6 was examined by Suryasarathi Bose and Mahanwar [10]. Seena Joseph *et al.* have observed the influence of the variations in fly ash content, particle size of fly ash, as well as the influence of the type of silane coupling agents on the properties of recycled polyethylene terephthalate/fly ash composites [11]. The effect of particle size and concentration of fly ash on the properties of polyester thermoplastic elastomer composites have been examined by Sreekanth *et al.* [12]. The correlation of the mechanical and structural properties of fly ash filled-isotactic polypropylene composites was studied by Dilip Chandra Deb Nath, Bandyopadhyay [13]. Furfuryl palmitate coated by fly ash used as filler in recycled polypropylene matrix composites were observed by Shubhalakshmi Sengupta *et al.* [14]. Nath *et al*. have observed the kinetics of non-isothermal crystallization in fly ash filled isotactic polypropylene (iPP) composites [15]. They have studied the structure-properties-interface correlation of fly ash/iPP composites also [16].

However, a limited literature is available on the particulate composites especially for the composites made from Poly Vinyl Chloride and fly ash. Khoshnoud et al. were studied the effect of the chemical composition of FA on the thermal, mechanical and microstructural properties of rigid PVC foams [17]. Two different types of FA were added separately to the PVC foam compound at low (6 phr) and high (40 phr) loadings to compare the effect of these particles on the properties of the composites.

Hence in the present study, the particulate composites made from PVC plastisol and fly ash are obtained and their thermal and microstructural properties are studied, and the results are analyzed.

Experimental

In this work, two different types of fly ash waste particles were used in this work. Red-brown FA waste particles were produced as a byproduct in the Instalation for Ferro-nickel production process (marked as FA-FENI), while the second type of grey FA particles were obtained from Oslomej coal-burning thermal power plant (marked as FA-OS), located in R.Macedonia.

Composite films based on Poly Vinyl Chloride (PVC) polymer and fly ash particles were prepared by solvent-casting method in 1,4-Dioxin with the total mixing time of 30 min. Plasticized PVC was used

as a matrix. Concentration of the fly ash varied in the range of 5, 10 and 20 %. The fly ash partices were treated with 2M NaOH and 1M HCl to fly ash ratio of 10:1 by weight.
The obtained composite samples were analyzed by SEM, FTIR, DSC, TGA/DTA and swelling test. SEM analysis were performed using FEI Quanta 200 FEG system. TGA/DTA measurements were performed using a Perkin Elmer PYRIS Diamond Thermogravimetric/ Differential Thermal Analyzer. The studied material was heated in the temperature interval of 25 ºC÷1100 ºC by heating rate of 20ºC·min^{-1} in the air atmosphere. DSC measurements were performed with a DSC system (Mettler Star) under N_2 atmosphere in the non-isothermal regime (heating rate = 10 K/min, cooling rate = 10 K/min). All specimens were prepared to be in the range of 8-9 mg weight. FTIR spectra were obtained using the PE Paragon system (64 scans were averaged at a resolution of 4 cm^{-1}).

Results and discussion

Chemical composition of both types of Fly ash used in the preparation of the PVC based composite films was analyzed and the obtained data are shown in Table 1. As it was expected, in the fly ash supplied from Oslomej dominant fractions were SiO_2 and Al_2O_3 oxides, while in the fly ash obtained from FENI, besides SiO_2, the oxides of Fe_2O_3 and MgO were in higher portions also.

Table 1: *Chemical composition of Fly Ash samples*

Elements	FA-OS [%]	FA-FENI [%]
SiO_2	50	37,5
Al_2O_3	30	1,8
Fe_2O_3	13	22,5
MgO	1,5	14,5
CaO	3,0	2,3
TiO_2	1,0	/
Cr_2O_3	/	1,0

Uniform filler dispersion in the polymer matrix materials is very important in order to ensure that there was a good interaction between both constituents that will result in good composite's properties. Scanning electron microscope (SEM) was used to take pictures of the powder materials to determine the general look of fly ash particles shape. Characteristic SEM microphotographs of FA are shown in Figure 1. As it is seen from Figure 1, the shape of fly ash is not regular and uniform. There are large and small particles which were expected due to the mixed composition of ash content.

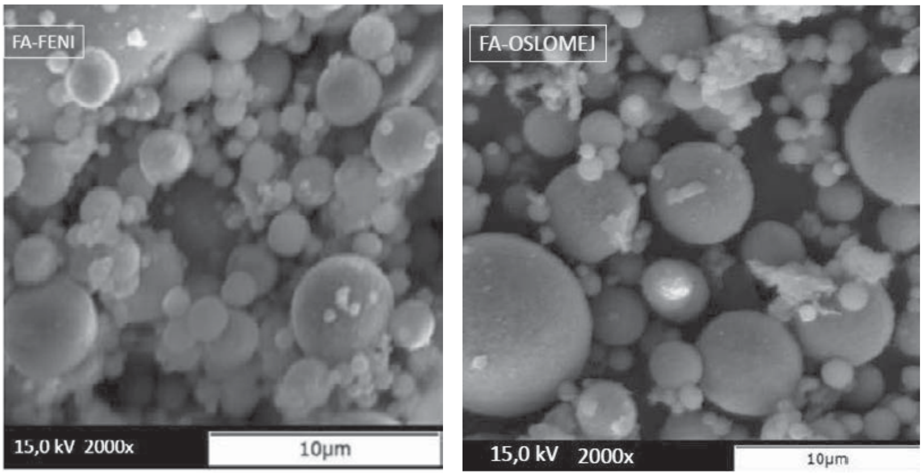
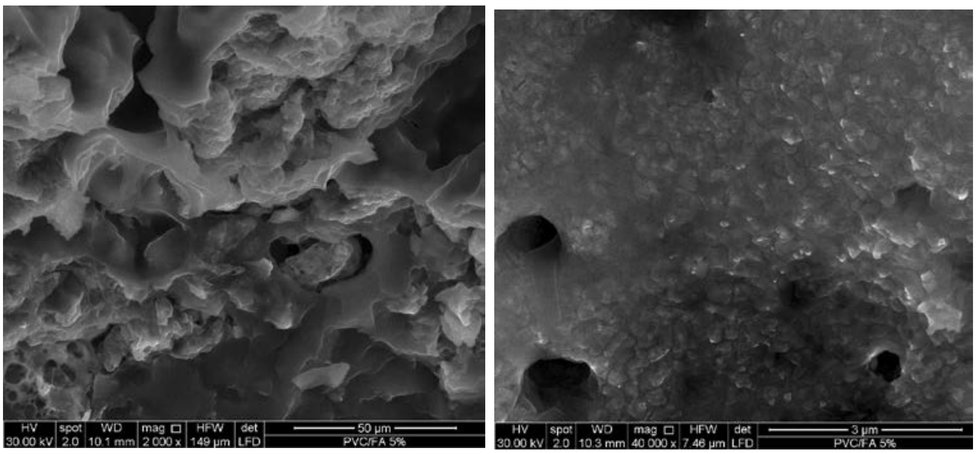


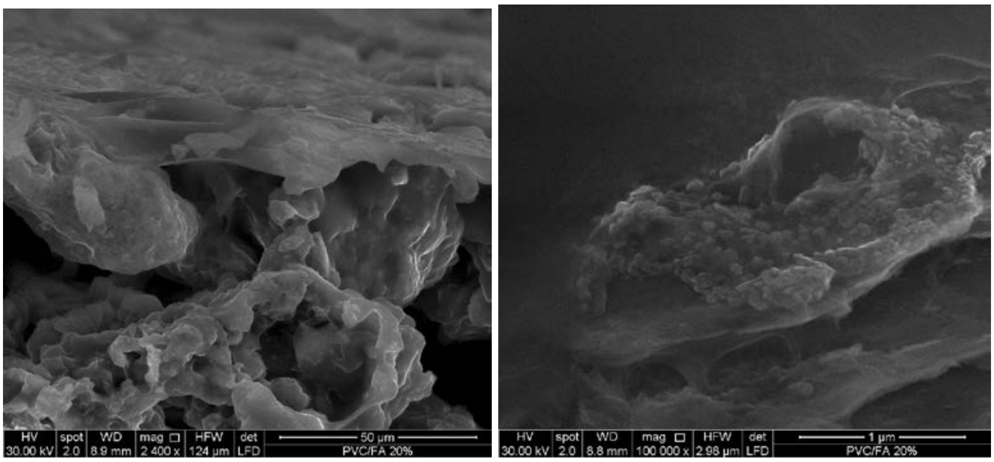
Figure 1. *SEM photos of Fly ash (x2000)*

SEM microphotographs of the obtained FA/PVC composites are shown in Figure 2 and Figure 3. The microstructural properties of the obtained FA/PVC composites confirmed region of well dispersed FA particles where the fly ash particles were tightly embedded and mechanically interlocked in the PVC matrix indicating strong interfacial interaction with the polymer matrix. However, particle agglomeration was observed in composites reinforced with higher amounts of fly ash. Besides information for the FA dispersion in the polymer matrix, SEM photos have shown that voids (holes) and micro pores were present in the obtained composites.



(a)(x2000) (b) (x40000)

Figure 2. *SEM photos of 5% FA/PVC*

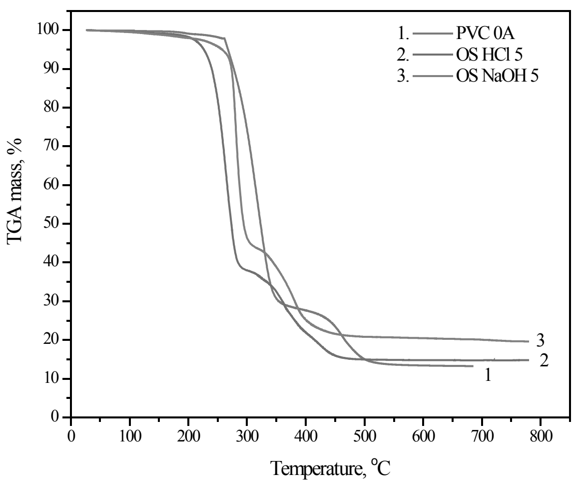


(a) (x2400) (b) (x100000)

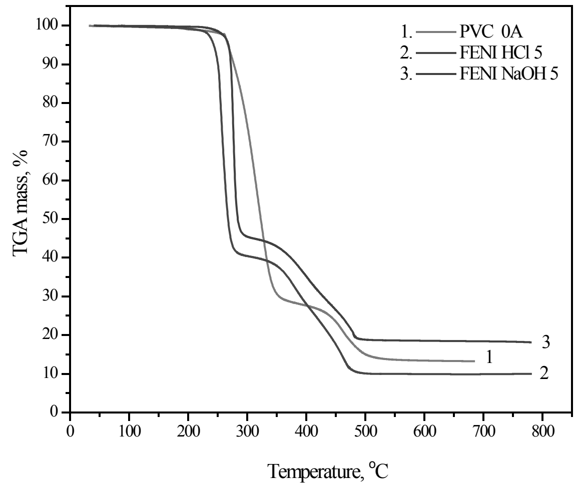
Figure 3. *SEM photos of 20% FA/PVC*

By increasing fly ash content, especially in samples with 20% FA, higher number of holes was evident which corresponds to filler debonding due to high filler loading and dewetting of fly ash surface with PVC matrix.

Characteristic TGA/DTA thermograms for FA/PVC composites with different type of FA, treated with HCl and NaOH, are shown in Figure 4 (Figure 4a for FA-OS and Figure 4b for FA-FENI). Thermal stability and all the other characteristic thermal parameters of the FA/PVC composites decreased in the presence of both types of FA. Lower values of primary thermal degradation temperature (T_d) were obtained due the HCL treatment of both types of fly ash waste particles.



a)



b)

Figure 4. *Characteristic TGA curves for FA/PVC composites with various treated fly ash;*

a) *PVC/FA–OS system,* ***b)*** *PVC/FA-FENI system*

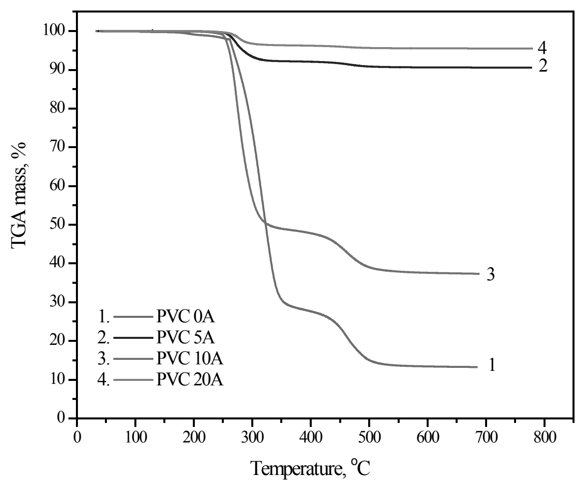


Figure 5. *Characteristic TGA curves for FA/PVC composites with various % of FA-content*

__Table 2.__ DSC data for FA/PVC composites

SAMPLE	T_g [°C]	T_{onset} [°C]	□C_p [J/gK]
PVC	58,7	49,1	0,326
5%FA/PVC	48,6	41,1	0,186
10%FA/PVC	42,8	34,5	0,064
20%FA/PVC	35,4	35,0	0,032

TGA thermograms for FA/PVC composites with different fly ash content (5, 10 and 20%) are shown in Figure 5. Increasing the fly ash content, it was found that thermal stability decreased. Fly ash particles have a higher thermal conductivity coefficient compared to PVC resin, therefore higher fly ash content can result in higher heat transfer which leads to thermal degradation at lower temperatures. The influence of fly ash content was confirmed by DSC thermal analysis also. The obtained data for the glass transition temperature (T_g) (shown in Table 2) of the studied FA/PVC composites confirmed that T_g decreased by increasing the FA content.

FTIR spectra for the studied FA/PVC composites are shown in Figure 6. FTIR spectra show the changes in the band of 1069 cm^{-1} and 1125 cm^{-1} which were connected with the structural changes in the obtained composites.

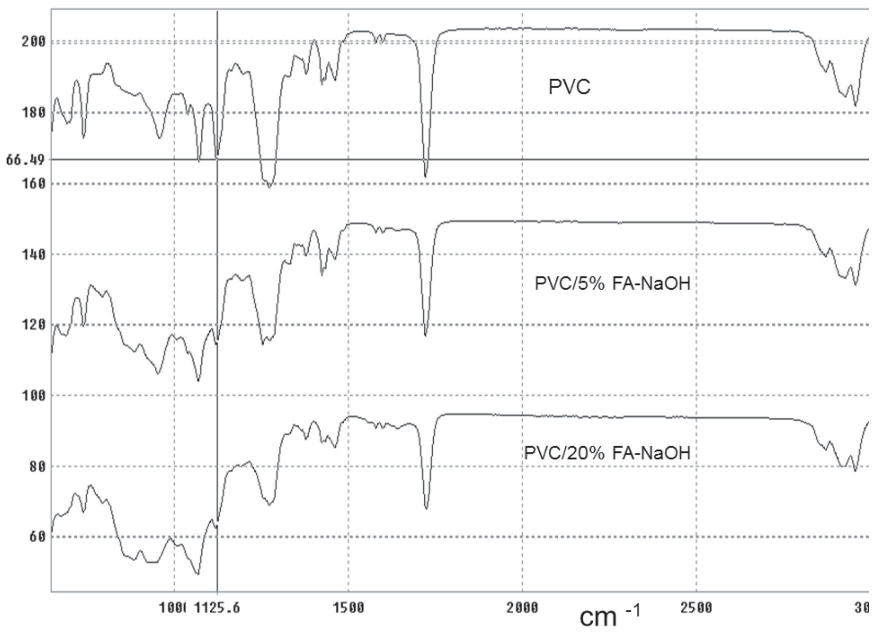


***Figure 6.** FTIR spectra of FA/PVC composites*

Generally, all the FA/PVC composites have shown higher swelling degree than PVC. Characteristic curves are shown in Figure 7 and Figure 8. Swelling degree increased by increasing the flay ash content (Figure 7). Higher values were obtained for composites with NaOH treated FA particles due to the hydrophilic character of OH groups. Swelling behavior was studied for both types of the used fly ash particles. Comparison of both type of FA confirmed that higher swelling degrees were obtained for FA/PVC composites with FA supplied from Oslomej (from coal power-plant).

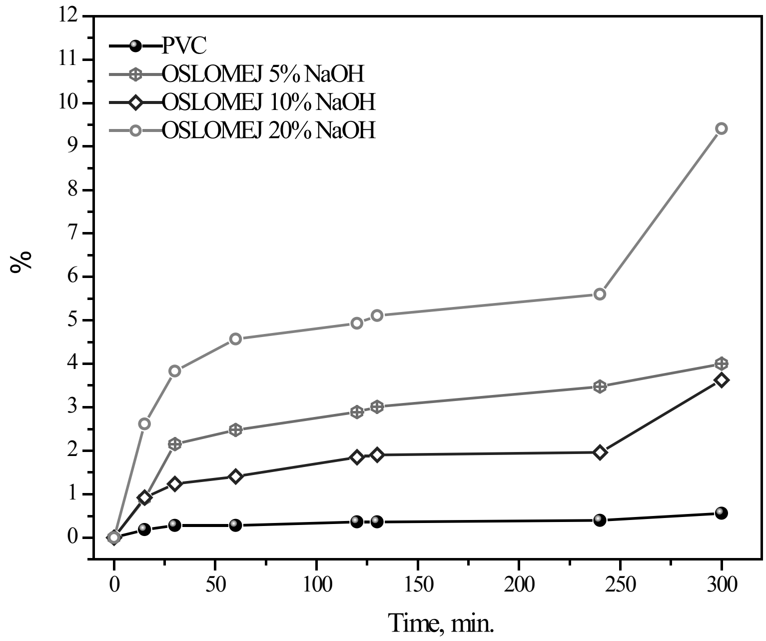


Figure 7. *Swelling behavior of PVC/FA OS-NaOH treated*

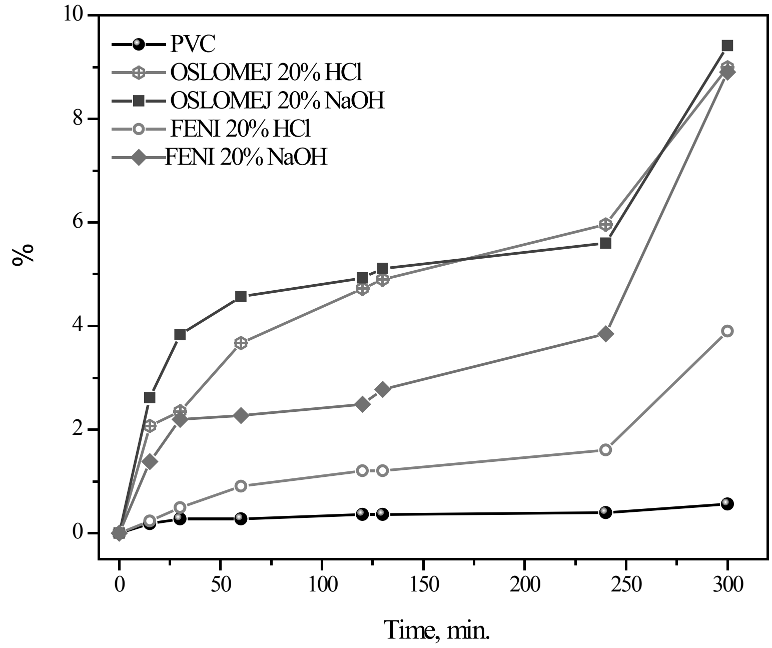


Figure 8. *Swelling behavior of PVC/FA FENI-HCl treated*

Conclusions

Composite films based on PVC and Fly ash were sucsesfully prepared by solvent-casting method. Plasticized PVC was used as a matrix and various concentrations of fly ash (5, 10 and 20 %). FA/PVC composite film-samples were prepared using two different types of FA (FA from fero-nickel production and FA from coal mine). The FA surface was modified by 2M NaOH and 1M HCl treatment. The obtained samples confirmed the influence of FA content on FA/PVC composite's thermal stability that was shown by TGA and DSC determined thermal parameters. Higher content of fly ash has resulted in higher % of swelling.

Acknowledgment: This research was performed within the Project "Environment protection of industrial waste through valorisation of metallurgical dust and slags in new environmental friendly polymer mortars and concretes" founded by Ministry of environment and physical planning of R. Macedonia (2012-2014).

REFERENCES

1. Demirbas A., (1996) Optimizing the physical and technological properties of cements additives in concrete mixture, *Cement and Concrete Res.*, 26, 1737

2. Polat M., Guler E., Akar G., Morogan H., Ipekoglu U., Cohen H.J., (2002*)* ,Feasibility of using fly ash, lime and bentonite to neutralize acidity of pore fluids, *J. Chem. Technol. Biotechnology*., 77, 372 , 2002.
3. Baba A., (2004) Investigations of leaching characteristics of ash wastes from thermal power planits in western Turkey, *19th World Energy Congress*, Sydney, Australia
4. Vassilev S.V., , Vassieva C.G., (2005) Methods for characterization of composition of fly ashes from coal fired power stations: a critical overview, *Energy Fuels*, 19, 1084, 2005.
5. Anandhan S., Sundar S.M., Senthil T., Mahendran A.R., Shibulal G.S., Extruded Poly(ethylene-co-octene)/ Fly Ash Composites-Value Added Products from an Environmental Pollutant.J. Polym. Res., 19, 9840-9851, 2012.
6. Deepthi M.V., Sharma M., Sailaja R.R.N., AnanthaP., SampathkumaranP., SeetharamuS.J., Mechanical and Thermal Characteristics of High Density

   Polyethylene— Fly Ash Cenospheres Composites. J. Mat. Des., 31,2051–2060, 2010.

7. Ra´thyIand KukiA. Borda, Preparation and characterization of poly(vinyl chloride)–continuous carbon fiber composites, J. Appl. Polym. Sci., 12,4,190–194, 2012.
8. GuhanathanS. SarojadeviM. Studies on interface in polyester/fly ash particulate composites. J. Comp. Interface, 11,43–66, 2004,
9. Fujino J and Honda T, "Measurement of the specific heat of plastic waste & fly ash composite material using differential scanning calorimetry", International journal of thermophysics volume 30, number 3, pp. 976-986, 2009.
10. Suryasarathi Bose and Mahanwar P.A, "Effect of fly ash on the mechanical, thermal, dielectric, rheological and topological properties of filled nylon 6", Journal of Minerals & Materials Characterization & Engineering, Vol. 3, No.2, 2004.
11. Seena Joseph, Bambola V.A, Sherhtukade V. V, Mahanwar P.A "Effect of fly ash content, particle size of flyash, and type of silane coupling agents on the properties of recycled poly(ethylene terephthalate)/fly ash Composites", J. Appl. Polym.Sci., 119 (1) 201-208, 2011.
12. Sreekanth M.S, Bambole V.A, Mhaske S.T, Mahanwar P.A, "Effect of particle size and concentration of fly ash on properties of polyester thermoplastic elastomer composites" Journal of Minerals & Materials Characterization & Engineering, Vol. 8, No.3, 2009.
13. Dilip Chandra Deb Nath, Bandyopadhyay, Aibing Yu, Darryl Blackburn, Chris White "Correlation of Mechanical and Structural Properties of Fly ash Filled-isotactic polypropylene Composites" World of Coal Ash(WOCA) , 2009.
14. Shubhalakshmi Sengupta , Kuntal Pal , Dipa Ray , Aniruddha Mukhopadhyay, "Furfuryl palmitate coated fly ash used as filler in recycled polypropylene matrix composites" , Journal of Composite Part B , pp. 42 , 1834-1839, 2011.
15. Nath D.C.D., Bandyopadhyay S., Blackburn A. Yu, D., White C., Novel observations on kinetics of non-isothermal crystallization in fly ash filled isotactic–polypropylene composites, J. Appl. Polym. Sci. 115, 1510–1517, 2010.

16. Nath D.C.D., Bandyopadhyay S., Yu A., Zeng Q., Das T., Blackburn D., White C., Structure–property-interface correlation of fly ash–isotactic polypropylene composites, J. Mater. Sci. 44, 6078–6089, 2009.

17. Khoshnoud P., Gunashekar S., Jamel M.M., Abu-Zahra N., "Comparative Analysis of Rigid PVC Foam Reinforced with Class C and Class F Fly Ash", Journal of Minerals & Materials Characterization & Engineering, 2, 554-565, 2014.