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Fly Ash in Optimized Composites Based on Recycled Plastics and Rubber

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1. INTRODUCTION

Recycling represents a sustainable solution for large amounts of waste rubber and plastics. While rubber recycling was long ago up scaled, thermoplastics recycling represents a problem and embedding them in large amounts in a rubber matrix represents a challenge. Adding certain ceramic powders strongly improves the mechanical properties and expands the applications but the three components should be compatible, therefore usually additives must be added[2, 6].

Most of the powders are metal oxides and their use was long before proved beneficial in rubber tiers manufacturing, as there are ZnO, TiO_2, CaO. The mechanical static properties are modified by adding these powders and the effect primarily depends on the strength of the organic-inorganic interface[4], thus on the composition, specific surface area and surface charge of the powder, along with the processing parameters: temperature, duration, etc.

Replacing these powders with fly ash represents available and sustainable alternative; fly ash has a rather large specific surface, and, according to the cola and burning conditions, it may have variable composition; usually, fly ash has a negative surface charge due to the predominant oxidic composition. A significant problem is that the ionic fly ash surface has a high wetting behavior, while rubber (and plastics) is hydrophobic, with very low surface charge. Therefore, building up interfaces based on electrostatic attraction is highly unlikely and thermal linking should be considered. The thermal process must be well controlled, targeting strong interfaces (visco-elastic regime) without decomposing the polymeric compounds.

The paper presents the optimization steps followed in developing composite materials fully based on recycled materials: rubber, poly-ethylene-terephtalate (PET) – polyethene (HDPE) and fly ash. The composites were prepared by compression molding. The composition, components' distribution, molding temperature and duration are optimized for obtaining composites with good mechanical properties tested by stress-strain, compression and impact (Izod) tests.

Fly ash with activated nano-surface (by alkali treatment) proved to develop uniform interfaces, with significant effect on the compression resistance and on impact. The behavior of the optimized composites at extreme outdoor temperature was investigated and the effect of fly ash is discussed based on the mechanical properties and on the changes in the material crystalline structure (XRD and DSC) and morphology (AFM). The effect of fly ash addition is also correlated with the surface energy, targeting further applications for outdoor products.

2. EXPERIMENTAL

Waste polymeric materials were used from: tire rubber, HDPE and PET bottles. These were washed and milled in particles with 1mm dimension.
Fly ash was collected from the CPH factory Brasov, Romania. The ash mainly consists of SiO_2 (53.7%), Al_2O_3 (21.60%) and Fe_2O_3 (9.56%) with a total percentage over 70% therefore, according to the ASTM standards[3], the fly ash is of type F. The unburned carbon (loss of ignition) amounts 3.8%.

For reproducible composites obtained by embedding the inorganic powder in the organic polymer matrix, fly ash should have rather constant surface properties. Still, the fly ash composition, crystalline structure and surface morphology significantly depend on the coal batch. therefore, a conditioning process is applied for leveling these properties. Based on previously optimized conditions[8], fly ash was washed under stirring for 48 hours in alkali solution (NaOH 2mol/L). During this process some oxides are removed (e.g. sodium and potassium oxides) and other oxides undergo a solubilization / reprecipitation process as SiO_2 does[7]. The fly ash with conditioned surface was dried at 120^{o}C for two hours, sieved and the fraction with average diameters between 100 and 200 µm was selected for composite preparation.

Previous studies[1] allow optimizing the composition and compression molding parameters for obtaining the composites. These are:

Rubber:PET:HDPE	= 60:35:5 (weight ratio)
Molding temperature	= 220…260 ^{o}C
Molding duration	= 60 min.

In the optimized composites, fly ash was added in a weight ratio of rubber:PET:HDPE: fly ash = 59.75:10:5:0.25, while the processing temperature was 240^{o}C and the duration 60 min.

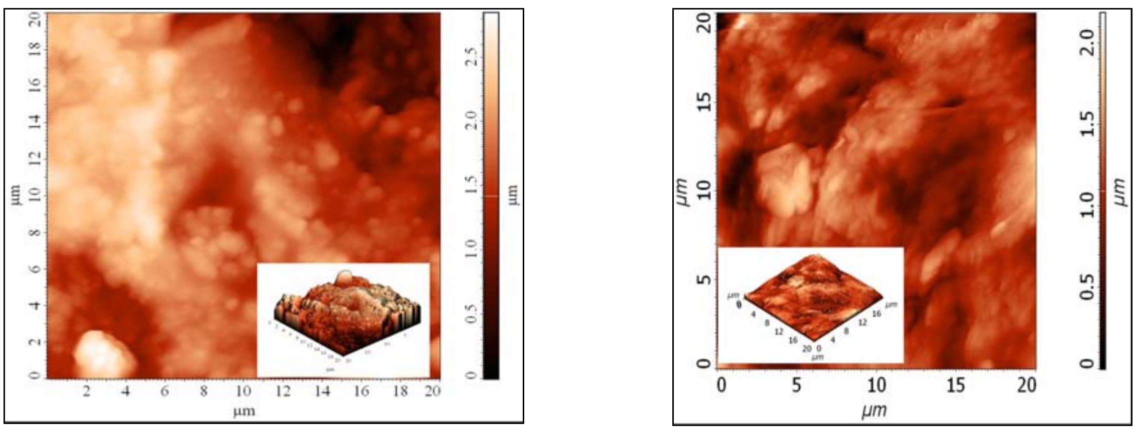
The composite samples were characterized in terms of crystalline structure by XRD (Bruker D8 Discover Advanced Diffractometer locked coupled continuous scan, a scintillation counter with 12800 steps, 2 seconds/step and a radiation with 1.5406 Å wavelength - Cukα1, at 40kV, 20mA) while morphology was investigated using an Atomic Force Microscope (AFM, NT-MDT model BL222RNTE). Static contact angle measurements were made in 1 second step (during 160 seconds), with the sessile drop method were recorded and analyzed using an OCA-20 Contact Angle-meter

(DataPhysics Instruments) to evaluate the surface charge. The thermophysical properties were evaluated by differential calorimerty (DSC, Perkin Elmer).

The mechanical properties of the samples were investigated for identifying the application range; stress-strain and compression tests were done a mechanical tester (Zwick-Roell, Z010) while Izod Impact tests used the IMPACT Galdabini device.

3. RESULTS AND DISCUSSIONS

The XRD pattern for the samples with fly ash show a crystalline degree of 29%, significantly higher comparing to the similar samples without fly ash, for which the correspondent value is 5%. The broad peak shows the large amorphous area but also confirm that the composite structure is organized around the nucleation centers which can be provided by the fly ash grain powder. The average size of the crystallite is 199.5nm, calculated using the Scherrer formula.



(a) Average roughness: 392.76 nm (b) Average roughness: 245.56nm

Fig. 1 AFM picture of the samples containing TiO2 (a) and fly ash (b)

This internal structure influences also the surface morphology. The AFM pictures of the samples containing fly ash and TiO_2 respectively are presented in Fig. 1. Samples without powder additives have a rougher aspect (depending on temperature the average roughness is 400…600 nm). This confirms that inorganic powders allow reorganizing the composite and developing stronger interfaces. It is also significant that this effect depends on the powder type, particularly on the polarity. Fly ash contains a larger amount of ionic oxides, thus has a surface with a larger (negative) charge which supports the development of stronger links with the organic polymer matrix.

Further studies were done to investigate the interface and to identify the type of bonds: physical or chemical. If chemical reactions occurred, than new, stable compounds should develop, with well defined thermo-physical properties: melting temperature, meting heat. The differential calorimetric studies showed two melting plateaus, corresponding to the waste HDPE and PET. Although the transition temperatures in the composite are almost constant, comparing to the waste components, the transition heat are much lower, indicating significant changes due to multiple, extended physical bonds at the interface. It is also to mention that the composite's glass transition temperature is close to rubber, confirming that the thermal behavior can be associated to the major component in the organic polymer matrix. All the thermo-physical data are presented in Table 1.

Table 1. Thermophysical data of the composite and of the organic components

Thermo-physical properties	**Material**			
	Rubber	**PET**	**HDPE**	**Rubber:PET:HDPE:Fly ash**
T_m [ºC]	22.93	244.41	127.73	123,89
				239,96
ΔH_m [J/g]	0.9	37.6	155.12	17,24
				12,31
T_g [ºC]	-50.52	-9.65	-	-58,05
ΔC_p [J/g ºC]	1.604	0.141	-	0,340

The composites based on recycled rubber, plastics and fly ash are low-cost materials that can be used in various products, for indoor and outdoor applications like pavement slabs, carpets, insulating walls, etc. Their particular application depends mainly on the mechanical properties. Therefore, the stress-strain, compression and impact strength were evaluated and the results are presented in Table 2.

Table 2. Mechanical properties of the composites with and without fly ash

Temperature	σ **[N/mm²]**	**E [N/mm²]**	**W la F_{max} [N]**
Rubber:PET:HDPE			
220	1.34	0.41	678
240	1.57	0.56	966
260	1.74	0.47	1308
Rubber:PET:HDPE:fly ash			
240	1.29	25.27	3473

By dispersing fly ash in the composite, very good compression resistance is obtained, much higher than the values obtained for the composites without the inorganic powder.

Considering the very low amount of fly ash (0.25%), this cannot be the result of simply mixing a much stiffer material in the polymer matrix, but it can be associated with the development of much organized/crystalline structures, heavily based on rubber and

PET. This assumption is supported by the impact tests: the initial Izod resistance was 12.3 kJ/m^2 and breaking occurs after 25 strokes. This is the prove of a quite rigid material, comparing with similar composites, containing TiO_2, where the initial resistance was of 8.8 kJ/m^2 and breaking occurred after 75 strokes.

The wetting behavior of the composite is also important considering the further applications. Contact angle measurements were done on the composites without and with fly ash, using water as wetting liquid. The data are presented in Fig. 2:

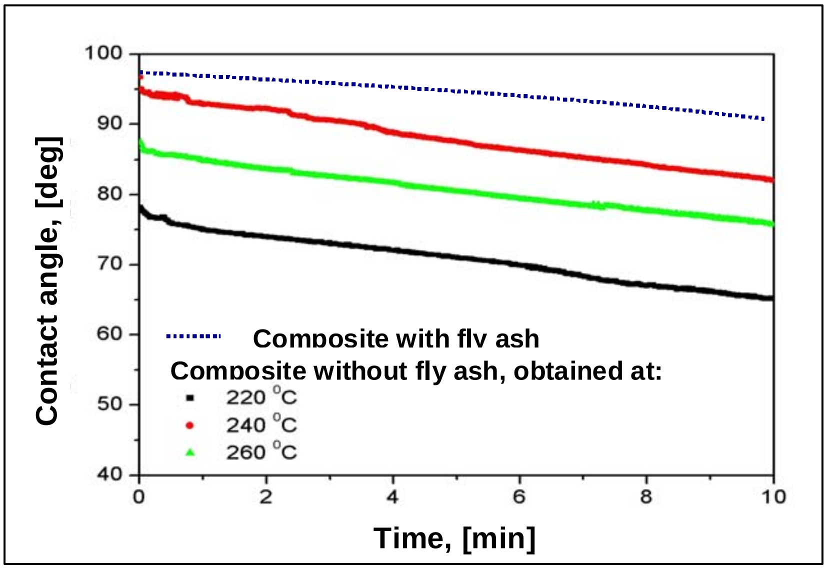


Fig. 2. Wetting behavior of the composites with and without fly ash

The samples without fly ash have lower initial contact angles, close or below 90^o, that correspond to an average wetting behavior. In time, with almost constant rate, the contact angle reduces due to a combined effect of the surface charge and of the surface porosity. Since the initial values are quite different and are influenced by the processing temperature, it may be concluded that variation in the samples' surface charge are the result of different oxidative degradation processes. The slope of the time variation in the contact angle values is almost identical for the samples without fly ash as result of a similar surface morphology.

A typical non-wetting behavior characterizes the composites with fly ash. The samples are more dense (the slope of the contact angle decay is lower), recommending it for outdoor applications.

The wetting process can be described by the pseudo-first and the pseudo-second order kinetic equations[5]:

$$ln\frac{\theta_t}{\theta_0} = -k \cdot t \qquad (1)$$

$$\frac{t}{\theta_t} = \frac{1}{k \cdot \theta_e^2} + \frac{1}{\theta_e} \cdot t \qquad (2)$$

Where: θ_t, θ_0 and θ_e represent the contact angle measured at the current time, initially and when reaching equilibrium and k is the rate constant. The kinetic parameters were evaluated based on the eq. (1) and (2) linneraisation ane are presented in Table 3.

Table 3 Kinetic parameters of the wetting process

Molding temperature [°C]	***Pseudo-first order kinetic***		***Pseudo-second order kinetic***		
	k	**R^2**	**k**	**θ_e**	**R^2**
Rubber:PET:HDPE					
220	0,0163	0,9965	0,0583	65	0,9990
240	0,0143	0,9976	0,0559	82	0,9994
260	0,0126	0,9981	0,0687	76	0,9995
Rubber:PET:HDPE:fly ash					
240	0,0124	0,9879	0,7341	64	0,9993

The results show that both mechanisms are well describing the wetting, as result of two parallel processes, running slowly (low k values). While the pseudo-first order kinetic corresponds to highly active surfaces, with a large amount of active sites, the pseudo-second order mechanism is related to average active surfaces. This supports the idea of heterogeneous surfaces and complex surface interactions during wetting. The pseudo-second order mechanism runs faster and is strongly predominant in the samples containing fly ash, proving once again the influence of this additive on the composite, even at low concentrations.

CONCUSIONS

Fly ash proved to be an efficient reinforcement agent in developing composites based on recycled rubber and plastics (PTT and HDPE). A low amount of fly ash (0.25%) dispersed in the composite acts as nucleation center and supports the self-assembly of the composite components, with an increase of almost three times in the compression resistance. The composites with fly ash have also a non-wetting behavior and a dense surface structure, therefore they are recommended for developing outdoor products like pavement slabs or anti-shock carpets for parks.

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