Accelerated Aging Test of Composites Based on Rubber, Recycled Plastics and Fly Ash

Anca Duta[1], Cristina Cazan[1]

[1]Transilvania University of Brasov, RTD Dep. Renewable Energy Systems and Recycling, 29 Eroilor, 500036 Brasov, Romania

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1. INTRODUCTION

The use of end-of-life products, for developing novel materials represents a trend supporting sustainability; plastics and tire rubber are among the most investigated materials. As second raw material, rubber preserve the initial properties but at lower values, therefore it can be reprocessed as such or by mixing with raw rubber; on the other hand thermoplastics (as poly-ethylene-terephtalate, PET) cannot be reprocessed (due to cross-linking – part of the manufacturing technology) therefore, their reuse can be done by embedding the in a composite matrix, e.g. using recycled rubber. The compatibility among rubber and plastics raises significant problems and compatibility agents should be used. Even so, these polymer-polymer composites have average properties and inorganic reinforcing agents should be used.

Fly ash, resulted from the CPH electrofilters can be used in developing organic/inorganic composites. Literature reports on using fly ash as reinforcing agent in composites having as matrix epoxy resins[2] or poly-vinyl alcohol[5]. Rubber – fly ash composites are also reported, using virgin and waste polymer material[3, 8]. According to the rubber:fly ash ratio, these composites preserve the elastic features (high rubber content) or the cement behavior (high content of fly ash).

Composites based on rubber, plastics and fly ash, with predominant elastic behavior were developed by using a third plastic waste (polypropylene, PP)[8], as compatibility agent and the data proved that there is an optimal (and low) amount of fly ash that has a beneficial effect on the mechanical properties of the composite. Replacing PP with low density polyethylene (LDPE) allow obtaining composites with good mechanical properties at high rubber content[9].

Composites fully based on recycled materials were developed using a rubber matrix, PET as filler, high density polyethylene (HDPE) as compatibility agent and fly ash as reinforcing agent. The optimized composites have good stress-strain properties and very good compression and impact resistance recommending them for outdoor applications[1, 10].

For using these composites as building materials (pavements, noise screens, impact dumpers) they must have a good aging resistance under common outdoor conditions (solar radiation, moisture, saline environment), preserving the specific mechanical properties. These types of tests are seldom reported although they are strongly recommended when targeting up scaling.

The paper presents the results obtained during the ageing tests performed on previously optimized composites containing rubber, PET, HDPE and fly ash[4]. The samples were subjected to accelerated aging tests under UV radiation, moisture, saline fog and water immersion and the modification of the mechanical properties are comparatively discussed with the samples stored, for a similar duration under normal conditions (25^{o}C, 25% moisture).

2. EXPERIMENTAL

2.1. COMPOSITE SAMPLES

The fly ash was collected from the Brasov CPH and the analysis proved that the silica, iron and calcium oxide content corresponds to the F class. To enhance the compatibility and obtain strong interfaces, the fly ash was conditioned by alkali treatment (48 hours, under stirring in NaOH 2mol/L solution) and the fraction 100…200μm was separated by sieving and further used.

The samples were prepared by compression moulding, at 240^{o}C, for 60 min. The composition of the samples is (weight ratio):
Rubber: PET : HDPE : fly ash = 59.75 : 35 : 5 : 0.25.

2.2. AGEING TESTS

Different ageing tests were performed by subjecting the composite samples, for 500 hours at:

- UV radiation (house made photoreactor, with 3 black light tubes, with emission in the range 340-400 nm, and maximum emission wavelenght $\lambda_{max(emisie)}$ = 365 nm);
- Saline fog (fog room VOTCH with temperature control);
- Immersion in deionized water;
- Immersion in 3.5% NaCl aqueous solution;
- Immersion in water-surfactant solution.

2.3. SAMPLE CHARACTERISATION

The samples were characterized before and after accelerate ageing.

The mechanical properties were investigated using a Zwick-Roel tester (stress/strain and compression) and the Galdabini device for Izod impact tests.

The contact angle measurements were used as a rapid and reliable test of the surface changes (charge and morphology) using a Data –Physics Instrumens device.

RESULTS AND DISCUSSIONS

Accelerate ageing influences the interfaces but, the initial effect is on the composite surface. Surface degradation, either chemical (oxidation) or mechanical, starts on the surface, especially on the highly energetic points (e.g. corners and edges) and is further propagated on the interfaces and boundaries. This is why, surface energy variations are investigated, as a primary hint for the modifications induced by ageing. The surface tension is the sum of two components (dispersive and polar), being predominant on non-ionic surfaces (the dispersive component), respectively on polar and ionic surfaces.

The two-liquids method[6] was used to estimate the surface energy, based on contact angle measurements of two liquids (water and NaCl 3.5%) on the composites surface.

The data are presented in Table 1, for all the ageing factors, comparatively to the vales obtained for the samples before ageing.

Table 1 Surface energy modification during ageing

Ageing Factor	Surface energy (mN/m)	Dispersive component (mN/m)	Polar component (mN/m)
Befor ageing	45,91	45,80	0,11
UV	21,85	3,23	18,61
Water immersion	28,65	8,46	20,19
DOWFAX immersion	107,77	106,93	0,84
Saline solution immersion	30,36	9,00	21,35
Saline fog	36,51	4,30	32,21

The data show that ageing usually results in decreasing the surface energy. This can be the result of increasing the amount of non-polar compounds or decreasing the amount of active loci: corners and edges. The data show that the polar component strongly increase, therefore the first assumption for the surface energy decrease cannot be valid.

The polar component increase can be the result of surface reactions, forming unsaturated compounds (even oxidized). The exception is related to the contact with surfactant solutions (DOWFAX) which has a completely opposite effect. The data could be linked with the surfactant strong adsorption on the composites components, blocking the ionic/polar sites and acting like a protective layer towards the working environment. It is also to notice that the strongest effect on the surface quality is registered after UV irradiation, when photo-chemical reactions are running.

The samples that were immersed in various aqueous media were tested for investigating the diffusion processes. Considering that there are no strong interactions (the composites being low polar), the Fick Laws was considered to apply in describing the diffusion process. The integrated form of the 2nd Fick Law, applied on uni-directional diffusion[7] is:

$$\frac{W}{C_\infty} = \frac{4}{\sqrt{\pi}}\left(\frac{D \cdot t}{l^2}\right)^{\frac{1}{2}} \qquad (1)$$

The overall adsorption was gravimetrically measured on dry samples, and the relative (%) weight increase was calculated using eq. (2):

$$\text{Absorption} = \frac{mass_{after\ ageing} - mass_{befor\ ageing}}{mass_{befor\ ageing}} \cdot 100\ [\%]$$

The data are presented in Fig. 1. Based on the linear part of the plots, the diffusion coefficients are calculated.

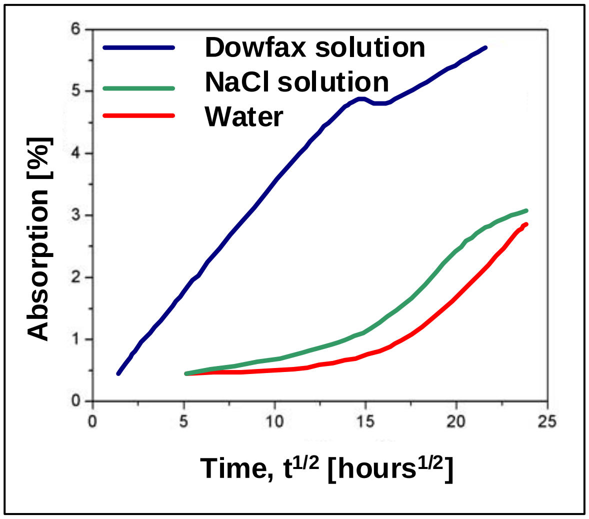

Fig. 1 Absorption during immersion

Diffusion coefficients, [mm^2/h]

Water: 1.046

DOWFAX solution : 0.573

NaCl 3.5%: 4.284

The data show high absorption with low diffusion rate, for solutions containing the surfactant DOWFAX. These apparent contradictory results can be explained by the surface processes, as confirmed by the energy data in Table 1. The result is that there is no longer depth diffusion, thus the composite's interfaces are protected. The hydrophobic layer formation is also confirmed by the linear shape of the curve, which is registered only when very low interactions are possible.

This is not the situation for the other aqueous media, when adsorption has almost identical values, proving that diffusion is favored by (micro)cracks and pores, and that chemical interactions are not likely. The rather high diffusion coefficient for the saline solutions raises serious concerns for the surface durability, especially for sudden temperature changes, and limits the composite applications in marine environments.

The mechanical properties of the samples before and after ageing are presented in Table 2.

Table 2 Mechanical properties of aged samples

Ageing Factor	Stress - strain				Compression		Impact
	F_{max} [N]	ε - F_{max} [%]	ε - break [%]	E [N/mm^2]	W - F_{max} [Nmm]	W - break [Nmm]	Resistance [kJ/m^2]
Befor ageing	129	163.65	179.65	25.75	3473.11	3863.32	12.9
UV	124	161.29	208.21	6.24	3184.88	4209.23	4.8
Water Immersion	144	207.74	252.66	7.77	4797.00	5991.52	5
Saline solution Immersion	145	212.39	240.06	11.97	4720.46	5476.49	12
DOWFAX Immersion	165	225.55	251.47	19.02	5592.79	6408.27	6.5
Saline fog	107	108.36	129.82	4.34	1911.00	2326.41	5.8

Stress strain tests show that ageing decreases the Young modulus (E), although the overall tensile strain is not significantly modified. This could be explained by an interface weakening, and the strongest effect is registered for UV and saline fog ageing. This is not surprising since these two factors are responsible for significant chemical degradation (UV) and enhanced diffusion (saline fog).

One exception is in the DOWFAX solution where, during ageing, the lowest changes in the tensile strain and Young modulus are obtained. The surfactant has also a strong and positive effect on the compression resistance. These data confirm that the surfactant adsorbs in/on the pores and cracks and is not removed after drying. This adsorption can also link to the substrate the possible degradation products/components which, in the other aqueous environments are washed out, in time.

The impact resistance is also affected by ageing but the samples maintain their impact properties even after 100 consecutive strokes. The sample immersed in saline solutions has almost similar impact resistance with the initial sample, due to the NaCl particles that crystallized, in time, in the pores. This behavior is also confirmed by the high compression forces.

CONCLUSIONS

Composites based on recycled rubber and plastics (PET and HDPE) were prepared by using fly ash as reinforcing agent. The composites were tests in accelerate ageing for identifying the optimal application fields of the novel materials. The most aggressive ageing factors were UV radiation (responsible for chemical/oxidative changes) and saline fog which, due to depth diffusion leads to destroying the interfaces.

Immersing for 500 hours the samples in water, saline solutions and surfactant solutions (DOWFAX) showed that the surfactant adsorbes on the surface and further acts as protective layer, thus improving the composite properties.

These results recommend the composite materials for indoor applications, for example as carpets in laundries.

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