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Mechanical analysis of powdered activated carbon-filled polyurethane foam composites for oil spill cleanup

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ABSTRACT

Polyurethanes (PU) occupy a special place in the plastics industry because of their great diversity. They can be linear, segmented, thermoplastic or cross-linked. It is possible to prepare a whole range of polymers with very different properties affecting many industries (rubber, paints and varnishes, plastics). Polyurethanes are very versatile materials that can be implemented by the main processes for specific applications. Interest in using polyurethane foams has been increasing recently, justified by easy implementation, low investment cost and relatively high surface area. The aim of this work is to study the reusability of synthesized PU-PAC (polyurethane-powdered activated carbon) composites, particularly for the study of oil spill sorption. Mechanical properties are assessed through permanent deformation tests in addition to other properties including resilience, Young's modulus and recovery rate after decompression.

Keywords: Polyurethane; Compression; Permanent deformation; Decompression; Young's modulus; Resiliency

1. Introduction

Polyurethane (PU) foam is commonly used to lighten and fill voids in metal structures. It also has excellent thermal [1–3] and acoustic insulation [4–6] properties, can absorb large amounts of liquids and exhibits a complex diffusion of light. From a mechanical point of view, it is characterized by good absorption properties of shock and deformation energy [7]. As a result of this broad spectrum of properties, the PU foam is used in many applications to provide comfort, thermal and phonic insulation, protection. Recently, PU foams have been used in a modified form for water remediation.

Several studies have been conducted to study the capacity of PU foams or PU-composite foams (clay, nano-composites and activated carbon) for the sorption of, as for example, organic matter, traces of metals [8], nitrogen and toluene [9] by PU foams, oil by oleophilic, hydrophobically modified, and nanoclay-modified PU foams [10–12], etc.

In this work compression–decompression cycles were carried out in order to study the damage behaviour of the PU-powdered activated carbon (PAC) composites and the possibility of their frequent use to clean up ocean oil spill by sorbing leaked petroleum hydrocarbons.

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1.1. Polyurethane foam preparation

The formulation adopted for producing the polymer matrix used for the preparation of PU foam is based on a polyol, isocyanate and other additives. The reagent mixture feeds a perfectly stirred reactor [13].

The PU-composite foam samples were prepared by varying the weight percent of the PAC added to the first PU formulation in order to increase the sorption capacity of the activated carbon-filled PU foam composite.

1.2. Compression–decompression cycles

Mechanical tests are generally used for the analysis of physical properties such as density, compressive strength, permanent deformation, tensile strength, resilience, tear resistance, airflow resistance, etc. For cellular materials such as polymeric foams, mechanical properties are often measured by compression tests. Thus, the sample is compressed between the two compression plates of the apparatus until an established deformation is achieved (Fig. 1).

The variation of the stress applied to deform the sample is measured by a force sensor and is recorded throughout the deformation. Through the analysis of the data, the stress values are visualized according to the deformation values to show the stress–strain curve.

A unidirectional compression–decompression cycle has two phases: the charging phase in a definite direction up to a final defined compression level and the discharge phase in the same direction. When the cycle number is greater than one, the compression–decompression test is said to be multi-cycle.

2. Materials used

The compression/decompression test was carried out using a Lloyd Instruments LF Plus 2745 (Ametek Company, Bognor Regis, Royaume Uni) traction–compression machine. The device comprises a fixed lower plate and a vertically movable upper plate. Loading is accomplished through the upper cylinder vertical movement down to the final defined compression level (for our case 80%). Unloading occurs in the reverse direction.

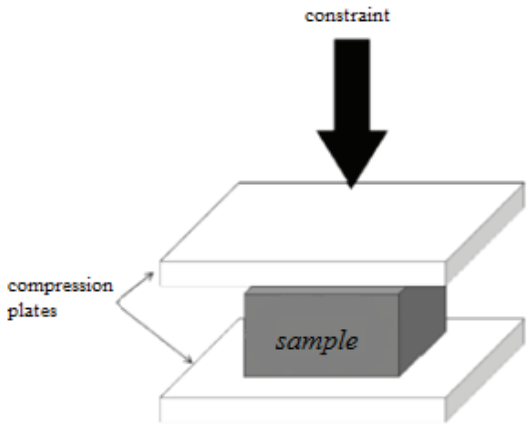

Fig. 1. Schematic illustration of a mechanical compression test.

3. Results and discussion

The addition of filler in the composition of the PU foam surely damages its quality [14–18] (destruction of the mechanical properties: problem of crumbling). Several formulations have been made in order to optimize the mass ratio of the PAC added to the PU matrix.

3.1. Preparation of samples

Only 3% and 5.81% PAC foam samples were studied as higher % PAC resulted in very fragile and friable foam as shown in Fig. 2.

The PU foams were prepared in virgin and composite form using different PAC mass percentages. Fig. 3 shows the images of the studied samples.

From the SEM micrographs of raw PU and PU composite, it can be seen that the structure of the raw PU cell was pentagonal and not ideal. The size of the cell ranges from 100 to 400 μm. In addition, micrographs of Figs. 3(b) and (c) show that the addition of PAC caused some destruction of the cellular structure of PU (Fig. 3(d)). It can be concluded that the maximum of PAC added to the PU structure for the hydrocarbon adsorption (petroleum) is 5.81% by weight.

Fig. 2. Poor quality foam samples with activated carbon content greater than 5.81%.

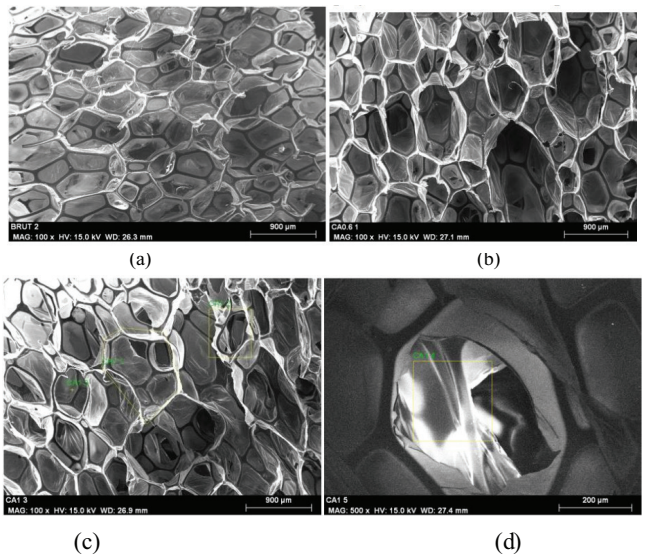

Fig. 3. Scanning electron micrographs of PUs; (a) in its raw form; (b)–(d) in its composite form (PU-5.81% PAC).

3.2. Mechanical analysis

The maximum force measured during the cycle should be as close as possible to the maximum capacity of the force cell (100 N) in order to maximize the signal-to-noise ratio at the acquisition level. Displacement and force sensors are integrated with in the machine. The number of cycles, the test conditions, the sampling period and the physical quantities to be determined are defined through the configuration window.

The prepared foams deform at low loading levels. Their stress response to uniaxial compression strain results in a hysteresis loop that is clearly distinguishable, with three behaviour zones (Figs. 4(a)–(c)). First, the material undergoes a relatively high stiffness which gives rise to a relatively steep initial climb up to the critical load (which determines the start of the plateau regime). It is usually in this case a linear elastic phase; this phase is due to the bending of the edges of the PU cells. As unloading occurs, the deformation of the sample is completely reversible. Then, the material stiffness decreases relatively and a plateau is observed. It corresponds to the presence of voids which cause the progressive crushing of the cells. It is associated with the plastic deformation of the structure and the rupture of the walls of the cells. Finally, the response becomes stiff giving rise to a steep climb again. As the deformation increases, the walls of the cells come into contact with one another and when all the voids are filled, the resistance of the foam increases rapidly, in proportion to the measured stress. This is the densification phase of the material. It corresponds to the complete crushing of the cells where the stress increases rapidly.

As the number of cycles increases, a progressive loss of the load resistance occurs, and a smaller loss between subsequent cycles is also observed. This loss is significant for the first and second cycles for all samples studied. It decreases after the fourth cycle for raw PU, after the seventh cycle for PU-3% PAC, and after the ninth cycle for PU-5.81% PAC.

At decompression, it can be noted that the response curves of the different cycles are roughly super imposed as a slight increase in residual deformation (permanent) with cycle number can be noticed.

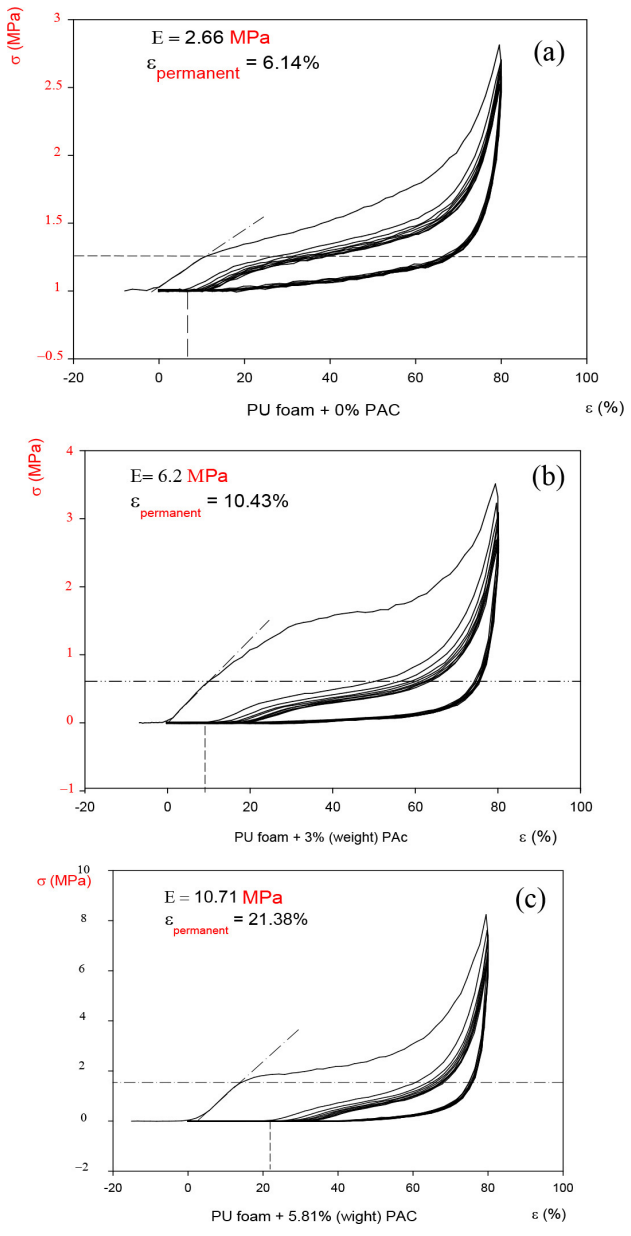

Fig. 4. (a)–(c) Stress–strain curves for the 3% and 5.81%-PAC-filled PU foam.

3.3. Permanent deformation

The permanent deformation corresponds to the limit deformation of the linear part (end of the elastic region). It increases with the amount of PAC added to the PU foam.

Fig. 5 illustrates the results of the residual (permanent) deformation determined graphically by the pure second cycle delay as a function of the PAC mass percentage of in the PU-PAC composites. It is observed that the permanent deformation increases with the amount of PAC added to the PU foams. It reaches 6.14%, 10.43%, 21.38% for the raw PU foam, the PU-3% PAC composite, and the PU-5.81% PAC composite, respectively. This is due to the amount of activated carbon added which makes the material more crumbly and more sensitive to mechanical stress.

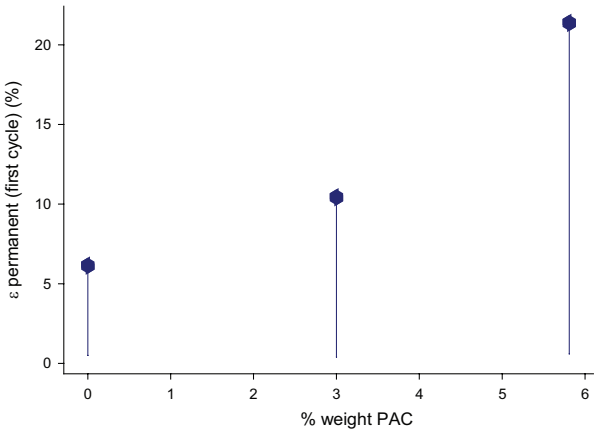

Fig. 5. Permanent deformation for the three PU-PAC samples.

3.4. Young's modulus

Young's modulus (E) (MPa) characterizes the elasticity of the material, it is determined by Hooke's law according to the following formula: $\sigma = E \cdot \varepsilon$, where σ (MPa) is the stress and ε is the strain.

Fig. 6 shows the variation of Young's modulus as a function of the mass ratio of the PAC added to the PU foams. It can be noted that the PU-PAC composites are more rigid than the raw PU.

Fig. 6 represents Young's modulus variation of PU-PAC composites with PAC content, graphically extracted from the initial slope of the curves shown in Fig. 4.

It is observed that the value of Young's modulus varies as a function of the mass ratio of PAC in the PU-PAC composite with 2.66, 6.2 and 10.71 MPa for the raw PU foam, the PU-3% PAC composite, and the composite PU-5.81% PAC, respectively. The increase in Young's modulus values is due to the increased density of PU-PAC composites.

3.5. Calculation of energy lost during the first cycle

The dissipated energy also called lost energy, during compression is calculated from the surface area of the hysteresis loop (Fig. 7). The results are shown in tabular form (Table 1).

It is observed from Fig. 4 that the dissipated energy (the area within the hysteresis loop) during the first cycle is greater than that during the second cycle; this reflects a reorganization of the internal structure of material after the first cycle. Overall, PAC-modified foams dissipate more energy than raw foam (Table 1). The lost energy is almost five times higher in the first cycle, showing that reorganization of raw foam structure is stabilizing rapidly (from the third to the fourth cycle) contrary to the composites (where the stabilization begins at the seventh and the ninth cycle for the 3% and 5.81% PAC composites, respectively).

3.6. Recovery rate after decompression and resilience

According to ASTM 36-39 [19], the calculation of the recovery rate after decompression and resilience is as follows:

$$\%\ \text{Recovery} = \frac{R - M}{P - M}.100 \tag{1}$$

$$\%\ \text{Compressibilty} = \frac{P - M}{P}.100 \tag{2}$$

$$\%\ \text{Resilience} = \frac{R - M}{R}.100 \tag{3}$$

where P, M, and R are the thicknesses of the sample in different situations, as shown in Fig. 8.

Figs. 9 and 10 show the variation of the two rates as a function of the amount of PAC added to the PU foam matrix for 10 and 100 cycles.

Overall, all three foam samples have high recovery and resilience values showing their good resistance to mechanical stress.

From the foregoing, it is noted that the PU foam has better physical characteristics than the PU-PAC composites which would explain that it is the most resilient and good recovery of its thickness during the 10th and also the 100th cycle. Concerning PU-PAC composites, although they represent good physical characteristics, their poor resilience

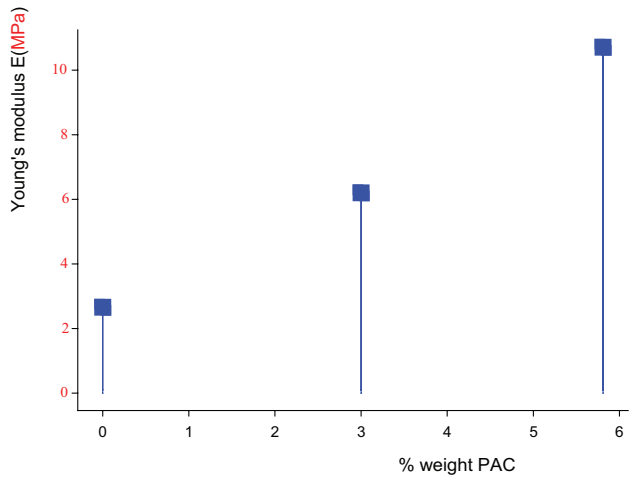

Fig. 6. Young's modulus as a function of PAC mass ratio.

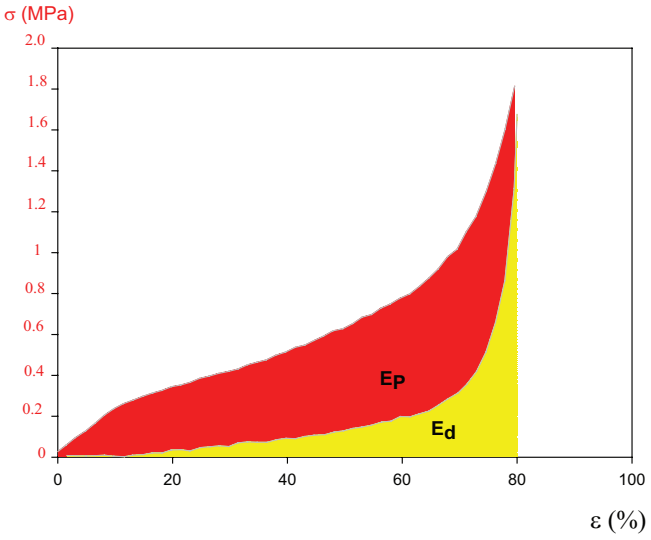

Fig. 7. Deformation and energy lost during the first cycle.

Table 1
Energy lost during the first cycle for the materials investigated

% PAC	First cycle		
	E_d (kJ/m^3)	E_c (kJ/m^3)	E_p (kJ/m^3)
0	25,520.29	48,339.98	22,809.78
3	13,433.77	120,889.60	107,455.83
5.81	28,452.71	206,761.05	178,308.34

E_d: energy density required for decompression; E_c: compression energy density; E_p: lost energy density.

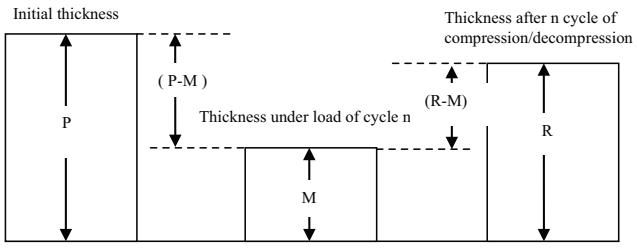

Fig. 8. Different thicknesses of sample under compressive test.

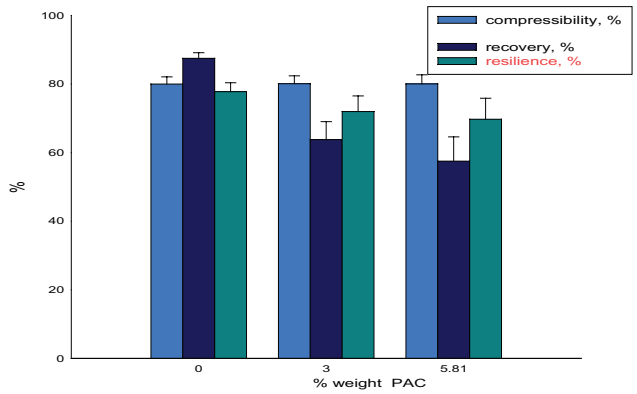

Fig. 9. Recovery and resilience rate for the 10th cycle.

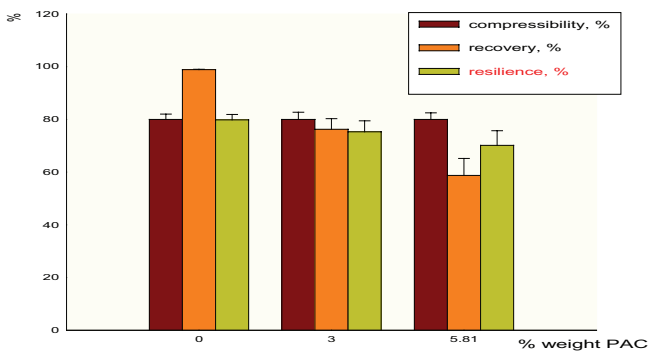

Fig. 10. Recovery and resilience rates for the 100th cycle.

could be explained by a poor regularity of structure but this is largely compensated for by the higher oil sorption capacity with 30.676, 20.166 g of oil sorbed/initial foam weight (g) for the 5.81% PAC-PU composite and the 3% PAC-PU, respectively, as compared with the corresponding value of 10.10 g for the raw PU [13].

4. Conclusion

To find the optimum of the mass ratio of the PAC added to the PU matrix, several formulations were made. Beyond 5.81% by weight of PAC in the PU matrix, the foams become very fragile and friable. 3% PAC- and 5.81% PAC-filled PU foams have a good hydrocarbon sorption capacity with 30.676, 20.166 g of oil sorbed/initial foam weight (g) for the 5.81% PAC-PU composite and the 3% PAC-PU, significantly higher than the value of 10.10 g/g for the raw PU.

The composites prepared were characterized by scanning electron microscopy to determine the pore size and assess the internal structure of the composites, and by mechanical tests to study their mechanical behaviour and reusability.

The mechanical tests and compression/decompression cycles carried out show the possible reusability of the 80%-compressed composites investigated. As the number of cycles increases, a progressive loss of load resistance occurs but a smaller loss between subsequent cycles follows. This loss is significant for the first and second cycle for all materials investigated but decreases after the fourth cycle for the raw PU, after the seventh cycle for the 3% PAC- and after the ninth cycle for the 5.81% PAC-filled PU foam. Future work will focus on the prediction of the dissipated energy as a function of the number of stress–strain cycles.

Finally, it can be concluded that the prepared composites can be used repeatedly for oil spill cleanup ensuring significant economy of sorbent.

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