Tribological Characterization of Modified Epoxy Systems

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A challenge of actual research in the field of epoxy resin composites is to find paths to modify the basic properties of these polymers but keeping unchanged their excellent mechanic properties when is about epoxy resins. One valuable way is to find appropriate solvents that are compatible with the used polymer and able to solvate specific salts such as using the solution to place metallic ions inside the polymer matrix. Such an attempt might be followed by solvent removal by various physical processes having as effect the presence of metallic ions in the polymer network with possible effects regarding the transport phenomena. There are some well-known solvents as 1,4-Dioxane, 1-Methyl-2-Pyrrolidinone and N,N-Dimethylformamide that can be used also as metallic complexes precursors and their effect on the properties of an epoxy resin should be known. Present study is concerning with the modifications induced by the use of above mentioned organic solvents together with glucose and starch as an attempt to create nano-structures inside the polymer. For this study three epoxy resins had been used and tribological behaviour had been studied on a TRM 1000 tribometer from Wazau (Germany).

Keywords: epoxy resin, glucose, starch, organic solvents, friction, wear

Because polymer composite materials can be produced on a large scale, their preparation methods have attracted much attention. Epoxy resins have a wide range of applications due to their remarkable performances [1, 2] and have been the subject of a multitude of patents and technical publication [3]. Generally, polymers have to show good wear resistance in order to be suitable for tribological applications. However, polymers have low-load carrying capacity and short running life when they are employed in tribological applications at high speed under heavy loads [4]. This is influenced by the working conditions, namely the temperature, the applied force, the relative speed of the polymer, surface interaction and solvents that are used to place the fillers into the polymer matrix. Epoxy resin is a commonly used thermosetting polymer matrix which already covers some of the demanded properties. However, because the polymer matrix must withstand high mechanical and tribological loads, it is usually reinforced with fillers [5, 6]. The fundamental understanding of synergy in tribological performance [7] among various functional fillers is essential for successful applications [8].

In particular, the use of organic solvents to place modifying agents [9-11] inside the polymer matrix had attracted increasing interest owing to their unique properties and numerous potential applications in the automotive, aerospace, construction and electronic industries [12-14]. In practice, special fillers or modifying agents are important for these purposes in order to improve the relatively poor load carrying capacity of neat polymers [15]. There are some well-known solvents as 1,4-Dioxane (1,4-D), 1-Methyl-2-Pyrrolidinone (NMP) and N,N-Dimethylformamide (DMF) that can be used as complexes precursors. Moreover, the tribological properties of polymer composites can be designed using other modifying agents – such as glucose or starch – that can be also used as precursors to obtain nano-structures inside the polymer matrix. Normally, an injection of glucose [16] and starch [17 -19] modified polymer is a process of great expansion and its effect, joining with different parts of (1,4-D), NMP and DMF, elements that are individually distinct, on the properties of an epoxy resin should be known.

1,4-D is a cyclic ether compound that is miscible with water in all proportions [20], moderately volatile and also abundantly and widely utilized as an ingredient in detergents as well as an extraction solvent and a stabilizer for chlorinated organic reagents [21].

NMP had been used as co-solvent in the petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbons. This cyclic amide further has excellent thermal and chemical stability and is used as absorbent of sour gases from crude natural gas [22].

DMF is a solvent with a low evaporation rate, useful for preparing solutions with a variety of hydrophobic organic compounds used in molecular biology applications [23].

Despite its scientific importance, very little information is available about the glucose and starch concerning with the modifications they induce when are used as modifying agents inside the polymer matrix.

The aim of the present work is to take organic solvents diluted epoxy matrix as an example to explore the role of starch and glucose in the friction of the composite.

Experiemntal part

Three epoxy systems were chosen mostly because of their different diglycidyl ether bisphenol-A (DGEBA) [24] content namely: Epiphen RE4020-DE 4020 (Bostik), Epoxy Resin C (R&G Gmbh Waldenbuch), and Epoxy Resin HT-2 (R&G Gmbh Waldenbuch). 1,4-D with a stated purity of 99.5% was purchased from Sigma Aldrich. NMP and DMF were also from Sigma Aldrich (with more than 99% and 99.8% purities, respectively). One of the two fillers, glucose (99.5%) was also purchased from Sigma Aldrich and starch was obtained from a local supermarket in Galati.

To create the composite materials first was necessary to determine the chemical compatibilities of components (matrix and solvents) in order to homogeneously disperse the modifying agents in the matrix. Glucose and starch solubility tests in the three organic solvents were run. So

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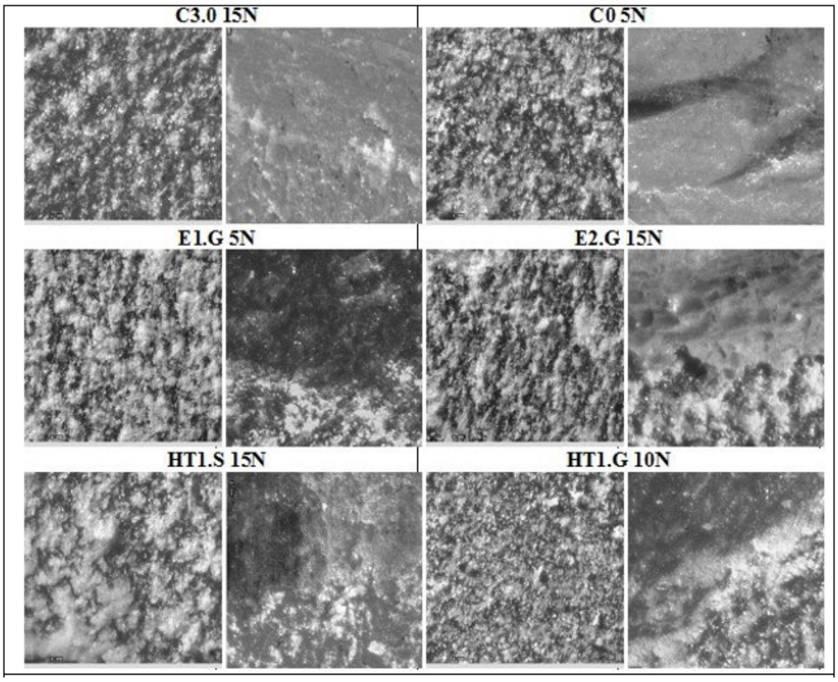

Fig. 1. Microscopic images of sliding surface (before and after the test)

we noticed that starch dissolved in each solvent without any special intervention only by stirring. In the case of glucose it took 15 min of stirring at a constant temperature of 50°C to be dissolved in DMF and 30 min in NMP. 50% concentration solutions of glucose and starch were obtained in the three solvents and these solutions were mixed with each resin such as to obtain a final material with a 9% weight ratio of modifying agent (solution). After stirring at 50°C for 15 min the correspondent amount of hardener was added and the stirring continued for another 10 min . There is an exception for this procedure namely the case of the mixture of HT-epoxy and the solution of glucose in NMP because of the thermal degradation of the mixture (when kept at 50°C) with an accelerated polymerization. In this case ambient temperature stirring was used.

These resins and the code designations for the test materials made from them are as follows: X0-(X=C, H, E) resin; X1 - resin modified with 1.4-D, X2-resin modified with NMP, and X3- resin modified with DMF; G-glucose; S-starch.

The friction behaviour of organic epoxy resins, solvents diluted epoxy resins and modified epoxy resins was investigated using a TRM 1000 tribometer from Wazau on pin-on-disk geometry, with the pin made of analyzed material and steel disk. The tests were performed a three different loads, with three sliding speeds in order to respect the same product load-speed on a distance of 1000m. The three regimes, denoted below as R1, R2, and R3, are characterized by a doublet (F,v) as follows: R1:(5N, 2m/s), R2:(10N, 1m/s) and R3:(15N, 0.66m/s). The friction coefficient and the wear rates of materials were investigated at ambient temperature. For each material three tests were run for each regime and the presented results are average values of the three tests.

Results and discussions

As it easily can be noticed from figure 1, no significant changes at the level of pin tested surface were induced by sliding on disk. The microscopic images were taken using an Olympus Microscope. Tribological test results, mass loss due to wear and surface observations are provided and discussed in the following section.

For all the diluted and modified materials the relative friction coefficient was evaluated with respect to the value of friction coefficient of corresponding resin and friction regime. In all the cases it can be noticed that softening the matrix (diluting with solvents or modifying with glucose or starch solutions) the values of friction coefficient are increasing.

Figures 2, 3 and 4 present the evolution of relative friction coefficient for C epoxy materials at the three regimes

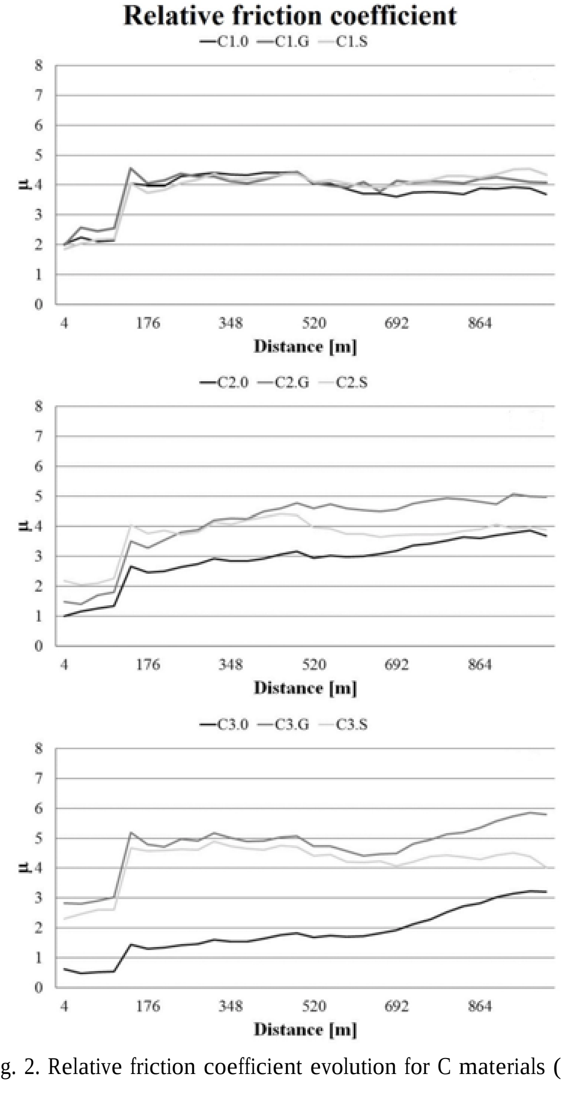

Fig. 2. Relative friction coefficient evolution for C materials (R1)

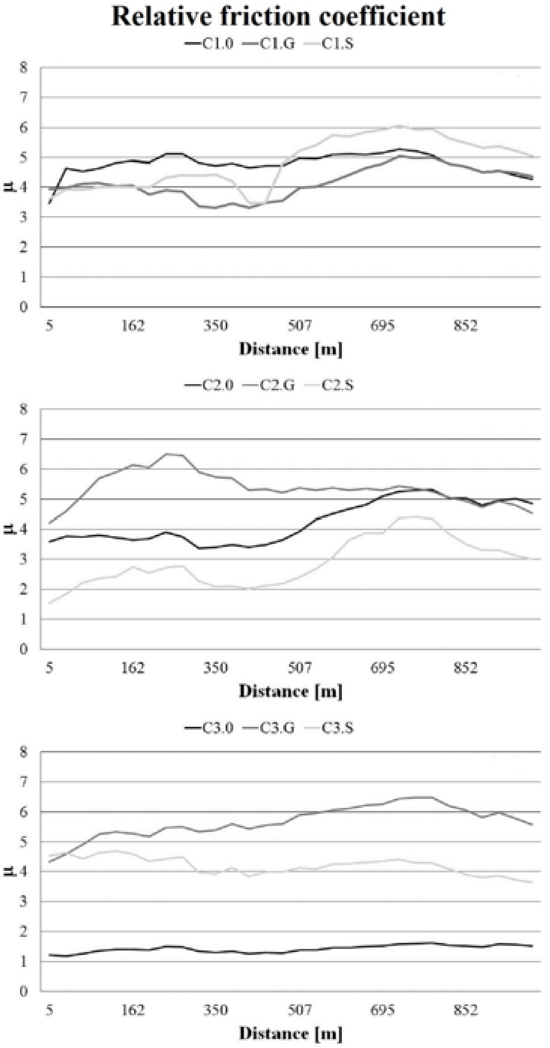

Fig. 3. Relative friction coefficient evolution for C materials (R2)

conditions. For these materials – as well as for all the materials, it can be noticed that the relative friction coefficient curve is ascending for the first part of sliding (up until the steady-state conditions are established) and, depending on solvent three types of behavior may be identified: all C1 materials are showing an increased value of friction coefficient (relative to C0) but after the transitional stage of sliding the values are remaining constant without respect to the presence of glucose or starch into the polymer; the C2 materials are showing a continuously increasing friction coefficient during sliding but with best behavior for C2.0; for C3 materials it can be noticed that the behavior of C3.0 is almost the same with the one of C0 and al the friction coefficients are increasing during the test. The E materials figures 5-7 noticeable instabilities are observable at the end of tests but these are disappearing when the load is increased. The E materials have almost the same friction behavior independent on the type of modifying agent denoting the fact that E resin is less affected by the agent presence than the other two resins. For E1 materials the friction behavior is the most stable denoting that the correspondent solvent (1,4-D) is the one that is not changing dramatically the polymer properties. Regarding H materials the situation is quite different since some of the samples had failed during tests. As it can be seen in figures 8-10, for some of the materials it was impossible to obtain the relative friction coefficient evolution curve meaning that all the solvents are denaturing the basic properties of the epoxy resin.

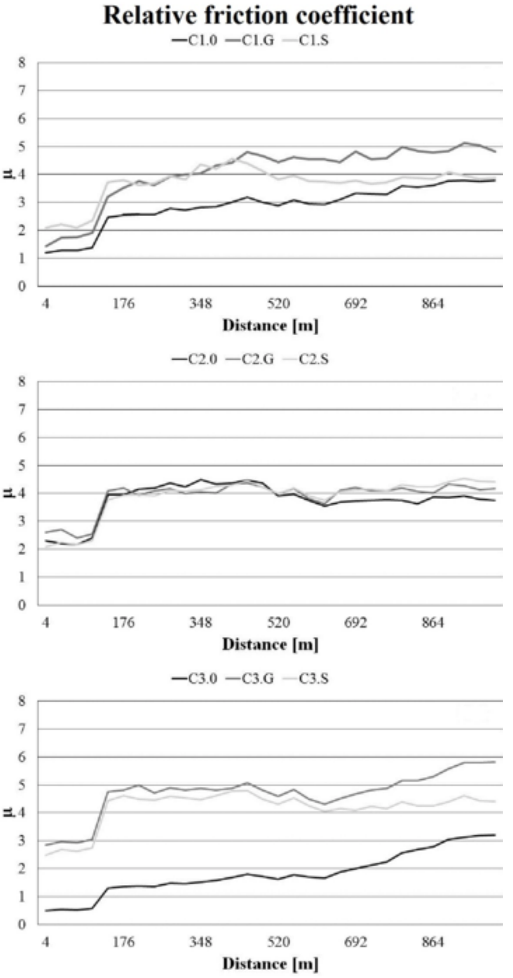

Fig. 4. Relative friction coefficient evolution for C materials (R3)

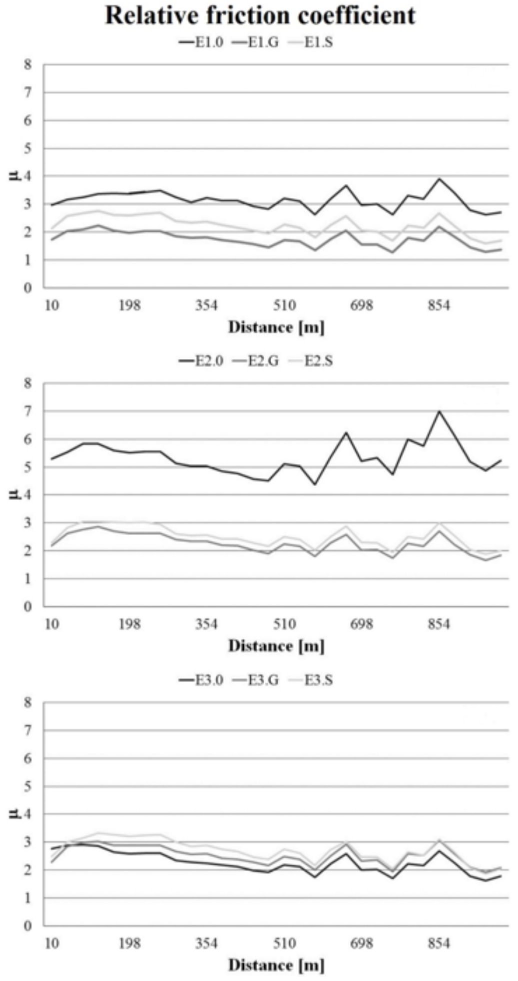

Fig. 5. Relative friction coefficient evolution for E materials (R1)

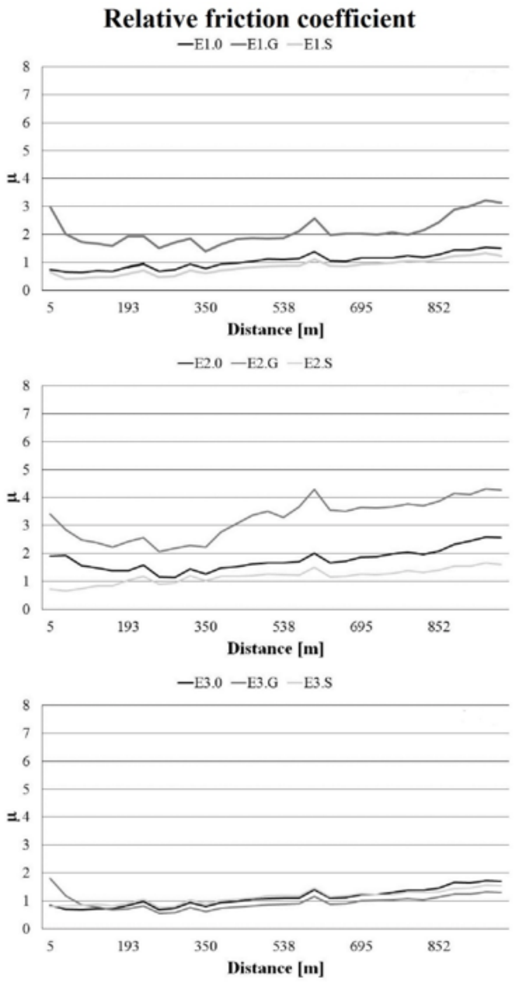

Fig. 6. Relative friction coefficient evolution for E materials (R2)

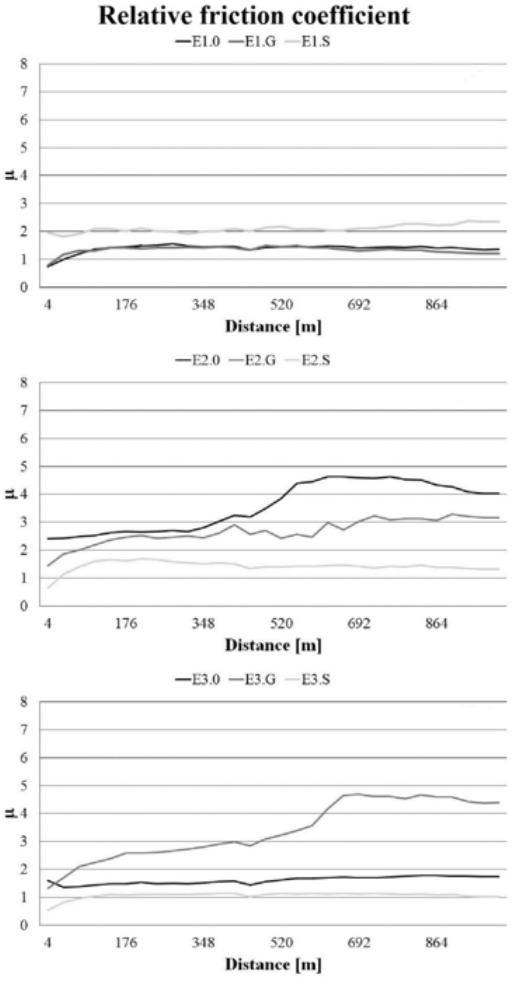

Fig. 7. Relative friction coefficient evolution for E materials (R3)

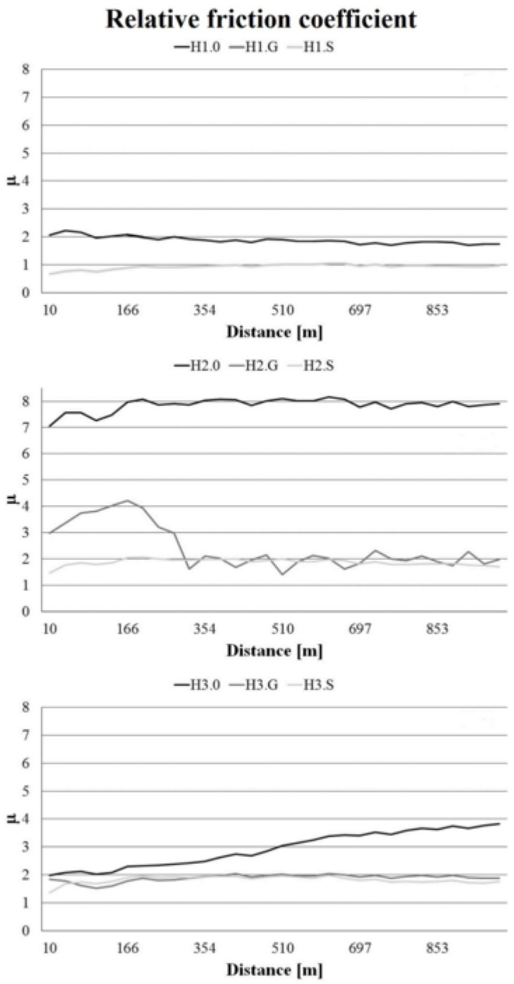

Fig. 8. Relative friction coefficient evolution for H materials (R1)

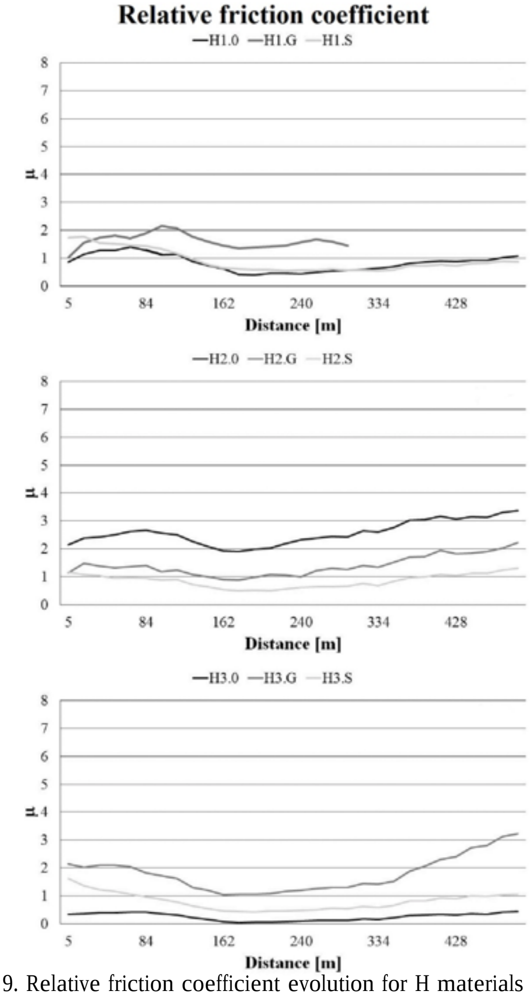

Fig. 9. Relative friction coefficient evolution for H materials (R2)

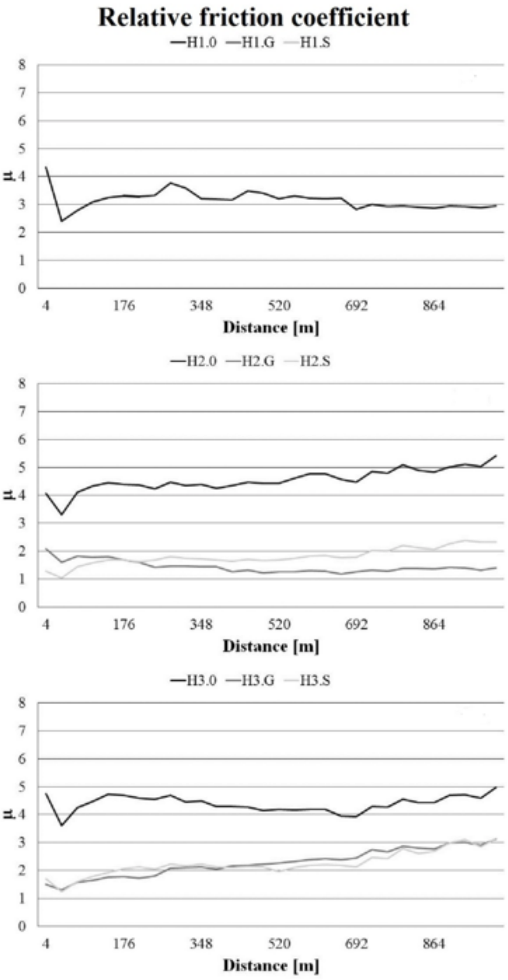

Fig. 10. Relative friction coefficient evolution for H materials (R3)

The specific wear rate (Ks) was calculated from the equation [25]:

$$K_S = \frac{\Delta m}{L \cdot D}$$

where Δm is the weight loss in grams; L is the load in Newton; and D is the sliding distance in meters. The specific wear rates for all tested materials are presented in table 1 (for C resin materials), table 3 (for E resin materials) and table 4 (for H resin materials). The highest mass loss for C resin system is recorded for C resin at 15N. For E resin systems and it can be observed an improvement in mass loss compared to C resin materials for all loadings. Regarding H resin materials it can be noticed that the highest mass loss is recorded to the force of 10N for 1.4-D glucose composite material. Surface observations are provided in fig.ure1 and, related to this, there are no significant differences between resins even if the mass loss difference appears. The vertical black lines are dividing the figure into two columns each one shows images of pin sliding face before (left) and after the test. The left column contains images of materials and regimes with the smallest weight loss while the right column contains images corresponding to materials and regimes with the highest weight loss.

Table 1

C resin material	**Wear rate [g/Nm]**		
	5N	**10N**	**15N**
C0	1.00E-07	3.70E-07	1.05E-06
C1.0	1.40E-07	1.10E-07	9.33E-08
C1.G	1.40E-07	2.30E-07	2.93E-07
C1.S	0.00E+00	2.00E-07	1.73E-07
C2.0	1.80E-07	1.40E-07	1.33E-07
C2.G	6.00E-08	1.20E-07	1.93E-07
C2.S	0.00E+00	1.40E-07	2.07E-07
C3.0	0.00E+00	4.00E-08	0.00E+00
C3.G	0.00E+00	4.00E-08	3.60E-07
C3.S	2.40E-07	3.10E-07	2.07E-07

Table 2

E resin material	**Wear rate [g/Nm]**		
	5N	**10N**	**15N**
E0.0	0.00E+00	0.00E+00	0.00E+00
E1.0	0.00E+00	0.00E+00	0.00E+00
E1.G	0.00E+00	0.00E+00	0.00E+00
E1.S	0.00E+00	0.00E+00	0.00E+00
E2.0	0.00E+00	0.00E+00	2.67E-08
E2.G	0.00E+00	1.00E-08	3.33E-08
E2.S	0.00E+00	0.00E+00	0.00E+00
E3.0	0.00E+00	0.00E+00	0.00E+00
E3.G	0.00E+00	3.00E-08	2.67E-08
E3.S	8.00E-08	3.00E-08	0.00E+00

Table 3

HT resin material	Wear rate [g/Nm]		
	5N	10N	15N
HT0.0	2.00E-08	0.00E+00	0.00E+00
HT1.0	0.00E+00	0.00E+00	1.33E-08
HT1.G	6.00E-08	4.30E-07	0.00E+00
HT1.S	0.00E+00	0.00E+00	0.00E+00
HT2.0	0.00E+00	1.00E-08	0.00E+00
HT2.G	1.00E-07	1.00E-08	6.67E-09
HT2.S	0.00E+00	1.00E-08	0.00E+00
HT3.0	0.00E+00	0.00E+00	0.00E+00
HT3.G	0.00E+00	6.00E-08	1.33E-08
HT3.S	0.00E+00	2.00E-08	1.33E-08

Conclusions

Presented results show the fact that the pure epoxies are more stable from the frictional point of view – because their rigidities, while all the modified polymers show higher values of friction coefficient. This behavior is explainable by the fact that the solvents are softening the polymers.

Friction and wear characteristics of three different epoxy resins concerning with the modifications induced by 1.4-D, NMP and DMF organic solvents together with glucose and starch were studied. The friction coefficients of the glucose and starch filled materials decreases compared with 1.4-D, NMP and DMF composite materials. In conclusion, the wear resistance of the studied epoxy systems cannot be enhanced only by using 1.4-D, NMP and DMF organic solvents, but together with glucose and starch there are significant improvements. The results are different from that of neat polymers under any of applied forces.

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