Improving the creep resistance for engineering thermoplastic materials

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ABSTRACT: The increasingly demanding applications of polymer based materials owing to their well established benefits over traditional materials ask for ever more improved performance not always achievable by commercial solutions.
For this reason, polymer scientists pay continuously attention to find new route for improving performance of available materials often by blending and/or compounding the same with tailored additives.
In line with this goal, special interest has been dedicated to further improve the high creep resistance of a thermoplastic semi-crystalline polyphthalamide (PPA).

Key words: Creep resistance, engineering thermoplastic, blend

1 INTRODUCTION

It is well established that thermoplastic polymers have gained an ever increasing room in high performance fields such as use in air- and spacecraft, in coating designed to protect metal and plastic surfaces from environmental attack or, more generally, to replace traditional materials such as metals.
In this light, rather than thinking towards new synthetic routes, promising results have been obtained by blending two or more organic commercial polymers and/or including small amounts of specific micro- or, recently, nano-sized inorganic additives as widely reported in the literature.
In line with this trend, taking into account that an usual deficiency of thermoplastics, seriously limiting their use, is their poor creep resistance, an engineering polyamide (Grivory GV5H) has been investigated and experimental work has been done to improve its creep behaviour.
Creep is a time dependent plastic deformation which occurs under stresses lower than the yielding stress of the reference material, so it is expected that any attempt aimed to constrain structural movements such as crosslinking and/or inclusions of rigid inorganic fillers could be useful to achieve the goal positively. Thus, effects of small additions of an epoxy oligomer (EP) and of a crosslinking agent (CA) on the creep behaviour of the considered matrix have been studied achieving satisfactory results especially in the former case.

2 EXPERIMENTAL

2.1 Materials

A thermoplastic semi-crystalline polyphthalamide (PPA) supplied by the EMS Grivory has been considered as a matrix material. Within the product assortment of this supplier, our attention has been concentrated on the Grivory GV5H, already used as an economic alternative to aluminium, magnesium and zinc alloys for die-cast components owing to their outstanding properties.
This formulation, including 50% w/w of glass fibers and characterised by good strength properties and higher modulus of elasticity, was oven dried before processing at 80°C for 8 hours.
The epoxy oligomer used in this study was a diglycidyl ether of bisphenol A (DER 331, Dow Chemicals Company, USA) and was dried under vacuum at 80 °C before use.
Finally, a crosslinking agent (CA) such as the poly (bisphenone A – co – epichlorohydrine) glycidyl end capped with an average M_n ~1,075 was purchased from Sigma Aldrich. In this case, a reactive extrusion process is allowed owing to the presence of terminal epoxy functional groups able to create inter- and/or intra-links among the macromolecular chains of the considered matrix.

Extrusion
Processing of the thermoplastic polyphthalamide and mixing of the dried components were performed with a Polylab Haake corotating twin-screw extruder (L/D=40/2.5) applying a screw speed of 150 rpm and a temperature profile 210 – 230 – 230 – 228 °C going from the hopper to the die.
The addition of both additives (liquids) to the matrix has been performed by using a syringe pump mounted on the second-last section of the extrusion path in order to prevent ay premature crosslinking of the same and, consequently, a reduction of their potentiality.
The interest has been confined within additive contents equal to 1 and 3% by weight.

2.2 Sample preparation

All extruded materials were pelletized and transformed in samples for subsequent creep tests by using an injection moulding lab machine. In particular, not having a specific mould for the present purpose, samples having the form showed in the following figure 1, have been produced.

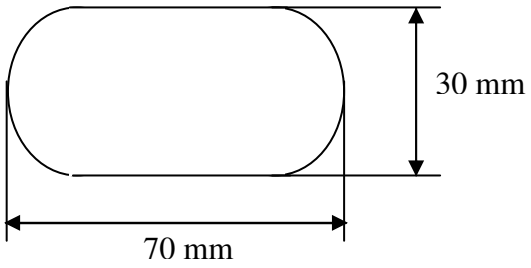

Fig. 1. Injection moulded 2 mm thick samples

Regarding the operative conditions, temperatures of 265 °C, 275 °C and 280 °C for the rear, central and front zones, were used respectively. The nozzle temperature was 60 °C. Pressures of 130 and 60 bars were used as injection and back values while, about speeds, filling operation and screw rate were set at 95 mm/sec and 100 rpm, respectively.
Finally, specimens for creep measurements have been cut from each samples, according to the reference standard.

2.3 Creep resistance measurements

Creep tests were performed at room temperature and load level equal to 35% of the strength determined from static flexural tests carried out at the same temperature.
A dynamometer Instron Mod 850 equipped with a 100 N load cell and a three point bending tool (figure 2) has been used to perform the tests.
The crosshead speed during loading of the sample was adjusted as to reach the desired stress level in a time of 5 s, as predicted by ASTM D2990-95 standard.
Experimental deflections (sweep), measured during the test at time intervals of 5 s, were monitored for 2 hours from the beginning of each evaluation.
Creep results of all compounded formulations were compared with analogous data evaluated on the matrix processed under the same experimental condition.

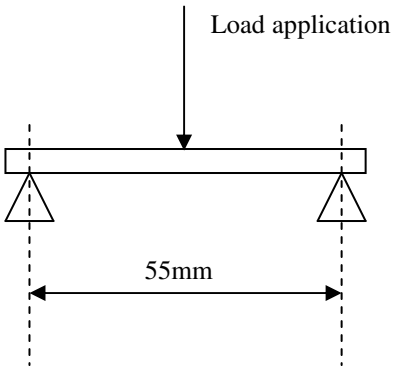

Fig. 2. Experimental setup for creep tests

Creep data reported herein were obtained by averaging results coming from at least five tests for each studied material.

3 RESULTS AND DISCUSSION

Experimental investigations were preliminarily aimed to enhance any effect of the involved processing operations on the creep behaviour of the investigated matrix.
In particular, creep results on injection moulded samples of neat Grivory GV5H prepared with or without a preliminary extrusion of the matrix were compared.
As clearly highlighted from the figure 3, the extrusion process causes a gradual increase during the test of the sample deformability that rises from 1.92 mm for samples obtained only by injection moulding to 2.13 mm when a preliminary extrusion of the matrix is carried out.
Undoubtedly, this is a sign of the occurrence of thermo-mechanical degradative phenomena that, of course, could be reduced optimizing the extrusion

parameters but that is impossible to avoid when a preliminary distribution of additives must be allowed.

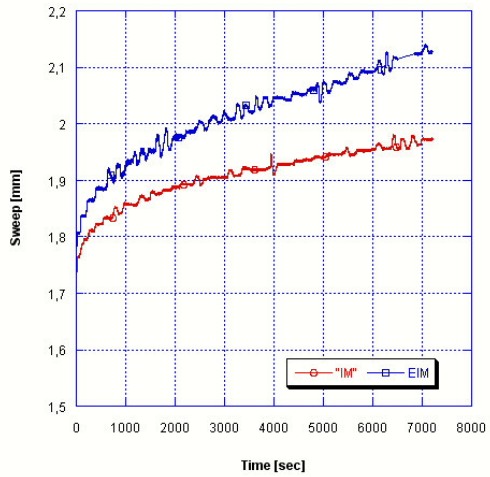

Fig. 3. Creep test results of injection moulded (IM) and extruded + injection moulded (EIM) Grivory GV5H samples

The effect of epoxy oligomer (EP) additions on the plastic deformation under constant applied stress is reported in figure 4 taking the extruded and subsequently moulded matrix as a reference.
In this case, a clear benefit is shown in presence of only 1% wt of the epoxy oligomer: a downward shift of the sweep versus time curve is shown with an increase of the central deflection of samples approximately equal to 0.22 mm all over the investigated time range

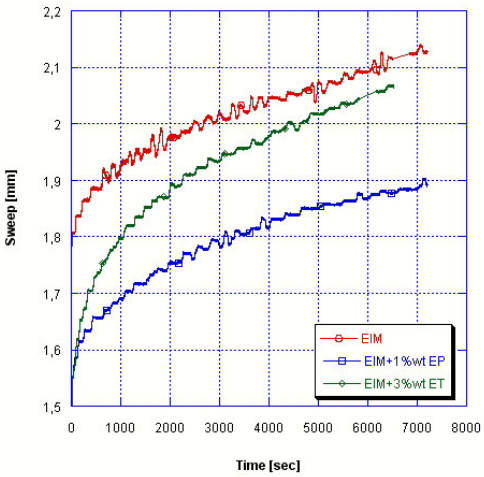

Fig. 4. Effect of EP additions on the creep behaviour of extruded and injection moulded Grivory GV5H samples

However, a further increase of EP seems to reverse the positive trend verified at lower contents of the same additive, probably because, owing to the necessary increasing of the epoxy oligomer flow rate the residence time appear to be no more enough to allow an additional crosslinking degree within the polyphtalamide matrix.
In this case, work is in progress to verify if reductions of the extrusion screw rate and/or of the temperature profile may lead to better creep results and to check how the same are influenced by the reactivity of different epoxy prepolymers.
Finally, time deformation of Grivory based specimens were compared in figure 5 at various contents of the crosslinking agent.

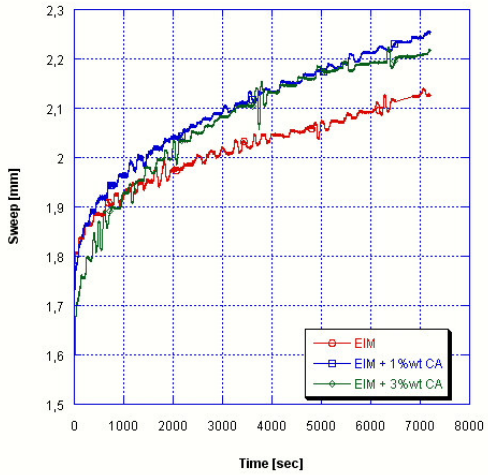

Fig. 5. Effect of CA additions on the creep behaviour of extruded + injection moulded Grivory GV5H samples

In this case, a worsening of the creep behaviour is observed for both considered compounds.
In particular, for an inclusion of 1% by weight of the CA, the initial deflection of compound samples is almost equal to that shown by the neat matrix. But, comparing this compound with the neat matrix, it is clear that the same parameter increases more quickly during the test reaching a value of 2.25 mm after 7200 s: 5.6% higher than the sweep recorded by the reference material specimens subjected to the same constant load.
Regarding the formulation containing 3% by weight of the CA, although a slight improvement of the creep behaviour seems to be verified at the beginning of the test with an averaged deflection of 1.69 mm with respect to the value recorded for the reference material (~1.79 mm), for times higher than 1000 s the measured central deflection of samples

exceeds that of the neat Grivory and, for times higher than 2000 s, creep curves of the two considered formulations appear to be overlapped.
Consequently, also in these cases it is clear that further research is necessary to optimize processing conditions. In fact, the cited worsening of the creep resistance could be again ascribed to poor crosslinking phenomena occurring within the matrix chains and/or to segregations effects. At this purpose, work is in progress to verify these hypotheses by structural measurements.

4 CONCLUSIONS

The effects of small contents (1 and 3% w/w) of an epoxy oligomer (EP) and of a crosslinking agent (CA) on flexural creep of an engineering thermoplastic polyphtalamide were investigated.
The results, besides enhancing adverse effects due to any degradative effects accompanying processing operations, showed a satisfactory behaviour in the case of the formulation containing 1% by weight of EP with a significant reduction of the central deflection parameter of specimens with respect to the matrix processed under the same conditions.
A general worsening of the flexural creep deformations was, instead, recorded for all other cases probably owing to the occurrence of additive segregation and, anyway, to the application of processing parameters not fully optimized.
Authors, although considering with satisfaction the experimental results obtained by now, owing to the outstanding properties characterizing the investigated product Grivory GV5H, will concentrate future interest to verify if any further improvement could be obtained by deepening complex but useful relationships among plastic deformations-morphology-structure-processing conditions.

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