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Microfillers – Advantageous Potential for White Goods Industry

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Summary: Market advantage of contemporary appliance product development heavily depends on the polymer materials and related fillers – e.g. micro-fillers. Presented and analyzed is washing machine, its vital product component - plastic tub. Namely, during the product life cycle it is exposed to the simultaneous and severe dynamic thermo-mechanical loads. Material selection for suitable polymer composite is conducted predominantly with time-dependency criteria – creep property at various thermo-mechanical conditions. Experimental validation and polymer material benchmarking is implemented on already regular polymer composites with mineral fillers from 4 different appliance producers ($PP + 40 \times CaCO_3$) on one side with the regular, on market accessible microfiller on other side. The overall study contain comparison of regular PP as basic, reference property in comparison with regular mineral fillers with/without technology processing and microfillers. All these data provide necessary and proper procedure path for the polymer product designer to conduct rational and reliable polymer material selection during polymer product development.

Keywords: creep; fillers; micro-fillers; poly(propylene); washing machines

Introduction

The appliance industry is considered to be traditional and mature branch, but in the past decades has experienced quantum leap in terms of product feature versatility accompanied with appealing design and user-friendly manipulation. Major influence comes from electronics, sensors and actuators, but above all by advanced (polymer) materials. The replacement of metal components with the polymer materials enabled cost effective production (assembly) and energy rational functioning - lower consumption with higher energy efficiency.

Presence of polymer materials in appliances and white goods industry in generally could be divided into the three phases:

- replacement of non-polymer materials, especially metal and alloys;
- introduction of additives and fillers (reinforcements) in the existing polymer materials;
- optimization of polymer material features with advanced polymer production (catalysation) and fillers (micro and/or nano fillers);

Among the other things, polymer materials are special due the possibility to enhance simultaneously many material features (properties) independently and we describe them as multifunctional materials. The polymer product designer face another specialty – the polymer materials have time-dependant properties, which are very sensitive on the environmental influences (e.g. temperature, humidity, thermo-mechanical loading).

Washing Machine and Poly(propylene) Composites

Among the all white goods products one of the most demanding are washing machines

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and their main technical functionality is effective laundry cleaning in the shortest possible time. They are made out of following components- Figure 1:[1]

- housing with supporting legs and bellow;
- electro-components – pump, driving electromotor, hydrostat and electronic circuit board;
- water distributions system – filter unit, hoses with dispersion unit;
- washing group – drum, tub, driving belt with wheel, counterweights;
- suspension system – springs and dampers;

Among these components, there are many made out of polymer materials – pump housing, control front panel with buttons, handle and cover of doors, dispenser unit with hoses, driving belt with the wheel and the most vital part – tub.

The most challenging to design is washing machine's tub due their very complex thermo-mechanical load profile during the washing machine operation.

Besides the static and dynamic load of (wet) laundry and drum, there is permanent static load of all suspended components (e.g. electromotor, counterbalances, drum). The permanent static load on polymer component couses phenomenon of creep, which is unfavorable and should be controlled via appropriate design and material selection.

The classical washing cycles is composed from 3 main activities – agitation (e.g. laundry distribution), speed up/down (s.c. ramp) and centrifuges (Figure 2). In the mean time is the water as well as laundry heated on specific temperature and cooled down with frequent fresh water exchange.[2]

Only balanced interaction of heating (temperature), mechanical action (agitation), chemicals (detergents) and washing time provide effective laundry cleaning. This is known as Sinner's cycle law and besides that, mechanical actions (agitation, centrifuge) has to take into account suppression of excessive washing machine vibrations. Smart control and actuators are supported with advanced IT software, what makes washing machines perfect to implement mechatronic product design procedure.[3,4]

Based on the practical experience, the most frequent thermo-mechanical load is in the area of temperatures from 25 °C up to

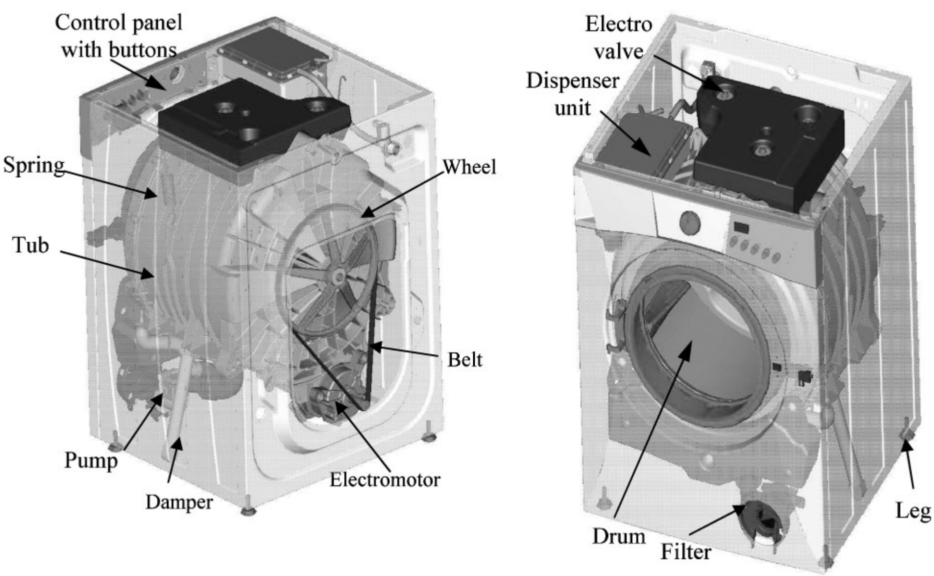


Figure 1.
Washing machine major (polymer) components.

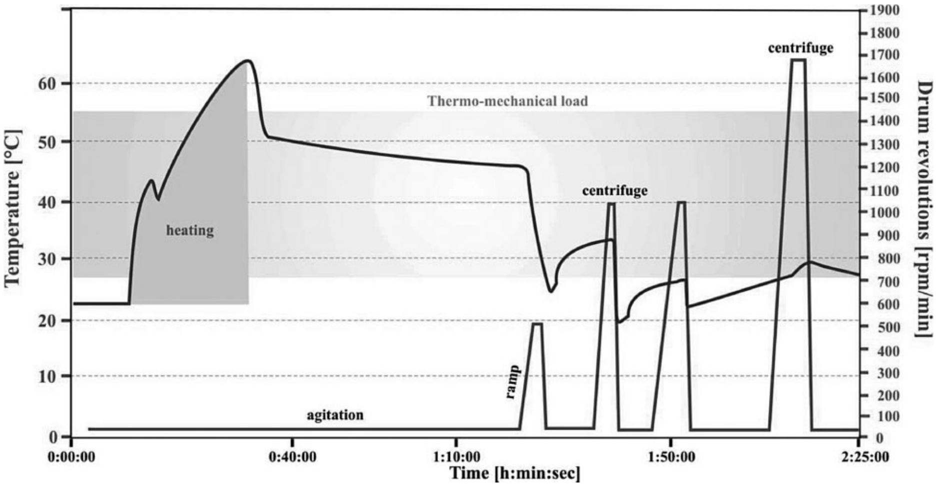


Figure 2.
Thermo-mechanical load during the classical washing cycle (cotton - 60 °C).

the 55 °C as well as forces with the drum revolutions from 700 rpm up to the 1500 rpm – Figure 2 (gray zone).

The executed forces on average washing machine (6 kg laundry with 11 liters water) make for the range angular velocity (700 rpm ÷ 1500 rpm) the range of dynamic forces – from 23 kN up to 105 kN. Therefore, the product designers have to focus most of their attention to the given (working) range for proper polymer tub design. The thermo-mechanical peaks are related to the temperature 95 °C (s.c. boiling washing program) and the ultimate drum revolutions – up to 2000 rpm, but for very limited time.

Polymer material has to anyway withstand short-term thermo-mechanical load (impulse loads) as well as long term loads (static), without geometry deformations or material degradations.

Poly(propylene) Composites and Evaluation of Polymer product Durability

In recent years, rapid growth and high consumption rates were predicted for various poly(propylene) composites, since they find applications in many areas such as automotive, home appliances, construction. The use of mineral fillers in the fabrication of poly(propylene) and other thermoplastic composites is mainly governed by price–performance relationships.

Poly(propylene) is a semi-crystalline engineering thermoplastic with balanced strength, modulus and chemical resistance. It is used in many outstanding applications in automotive industry, appliances and other commercial products, where creep resistance, stiffness and toughness are critical properties along with the weight and cost savings. Common way to effectively achieve improvement of mechanical properties is with the inorganic particulate fillers and particularly is enhanced the toughness.[5]

With the high particle volume fractions (30%÷50%), the processing of the material often becomes difficult, because the inorganic filler has a higher density than the base polymer and then the overall density of the filled polymer is also increased. Therefore the advantageous property of polymers for a good processing and lightweight is lost. To overcome this drawback, desired is composite with improved properties and lower (inorganic) particle concentration. This has been achieved with the micro- and nanocomposites, which gave to the poly(propylene) composites broader application opportunities.[6]

Another conclusion is, that particle size, matrix dispersion and shape of fillers play important role to enhance polymer composite properties and also became the subject of scientific interest since the end of the last century. Various materials of the same polymer product geometry may respond differently under identical external effects. This is very often attributed to the inherent constitution of the materials as rational way of rational (cost-effective) polymer product enhancement.[1,5,6]

The thermoplastic polymers, as viscoelastic and time-dependant materials, have another disadvantage - relatively poor creep resistance, which is unfavorable to their application as structural materials. The creep phenomenon is time-dependant deformation, which takes place under stress lower then the yielding strength of materials. In real (industrial) environment the polymer products are very often exposed during their life time to the constant load (creep) or to the constant deformation (relaxation).

Research works on all-PP composites has shown so far that the creep behavior PP/PP composites depends strongly on stress, temperature, void content, (fiber) loading, and (fiber) dimensions.[6,8]

This issue opens very important issue for the polymer product design engineer:

- proper testing technique for prediction polymer product durability (or reliability) during the life cycle;
- evaluation of experimental data and benchmarking from various samples (materials);

In industrial environment are available many standardized durability tests, but infrequently applied and used on a comparative basis only.[10]

In general, durability test are accelerated tests which are based either on Arrhenius approach (e.g. IEC 216) or Williams-Landel-Ferry (WLF) model for time-temperature superposition (e.g. ISO 11346 - revision).[11,12,13,14,15,16] These durability test are generally applicable in appliance industry, energy (cable insulations) and even paper industry.[17]

Already by definition an accelerated test requires that the degrading agent or agents is present at a higher dose than that to be seen in service (e.g. temperature). Modeling degradations process (e.g. product's life time) means to obtain a function for the rate of change of the parameter (e.g creep) with the level of the degrading agent (e.g. temperature).

Since we are focused on the washing machine polymer tub, there has to be analyzed time-dependant behavior under constant load at different temperatures. This is caused by components, which are hanged on the polymer tub (e.g. counterweights, electromotor).

The standardized tests, the tensile creep tests is already specified, where the sample is placed under load by a static force and the deformation caused by this force is measured as a function of time.[18] The creep tests are carried out at different levels of stress and sometimes at different temperatures or relative humidity levels. It has been proven, that the tensile test can be carried out more reliably then compressive and bending creep tests.

Why is WLF method more present in industrial application than the Arrhenius approach is because of following features:[11]

- with computer help WLF is easier to implement,
- does not need to specify a measure of reaction rate,
- to make any assumptions when interpolating between points and

more versatile to produce predictions in terms of time to reach an end point.

To describe creep phenomenon is used either creep strain, but very common is material function – creep compliance - $J(t,\sigma(t),T)$:[16]

$$J(t,\sigma(t),T) = \frac{\varepsilon(t,\sigma(t),T)}{\sigma_0} \quad (1)$$

where t is creep time, $\sigma(t)$ real stress, σ_0 initially applied stress, T temperature, and

$\varepsilon(t,\sigma(t),T)$ creep strain dependent on creep time, real stress and temperature.

For the case of small deformation, the real stress is normally considered as the same as initial stress and thus the strain is proportional to the initial stress:[16]

$$J(t,T) = \frac{\varepsilon(t,T)}{\sigma_0} \text{ or } J(t,\sigma(t),T) = J(t,T) = c \cdot \varepsilon(t,T) \qquad (2)$$

where c is the constant.

The creep test is performed at identical stresses and the shifting procedure excludes corrections for physical ageing and other effects. The problem with this procedure is that there is considerable variation between specimens in the initial strain which, coupled with the small slope of the creep-rupture diagram, can lead to large errors in shifting.[10]

This is overcome with the 'stepped isothermal method' (SIM). The temperature of a conventional creep test on an oriented polymer is raised in sharp discrete steps, which should have intermediate annealing and the strain measured – Figure 3.[19,20]

The intermediate annealing is necessary to clear the load history from previous temperature step. Otherwise, the annealing procedure is very often applied at the beginning of material test to erase previous thermo-mechanical history. This is done either to establish same reference conditions for the testing samples or to evaluate only material properties without previous processing modifications. At the end of the material test annealing is conducted only to set the sample at the starting condition.

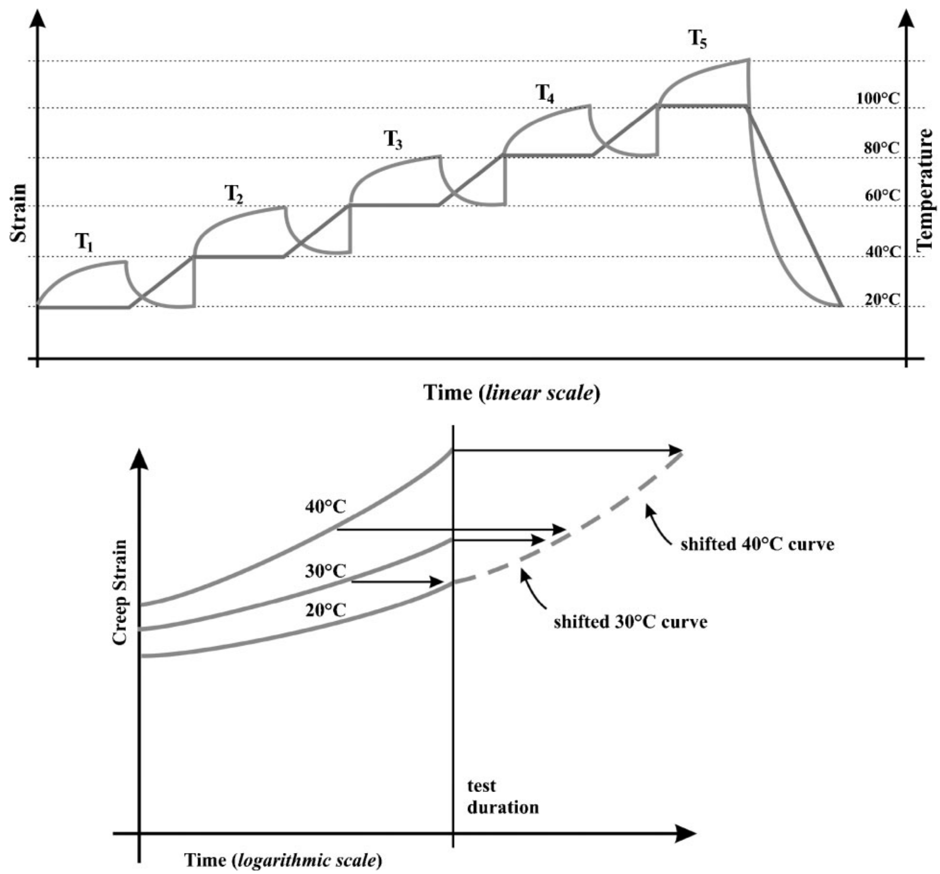


Figure 3.
Stepped isothermal method and time-temperature shifting.

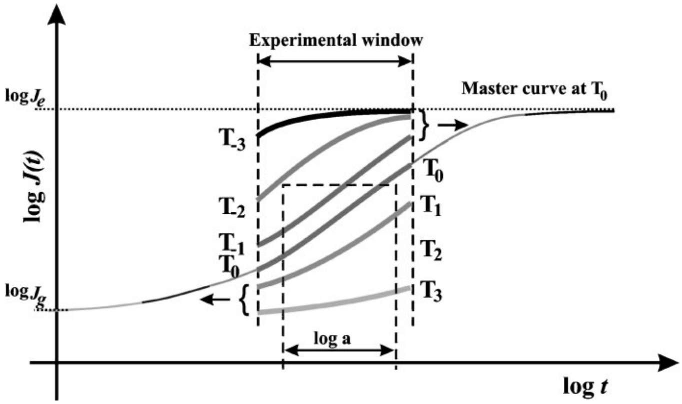
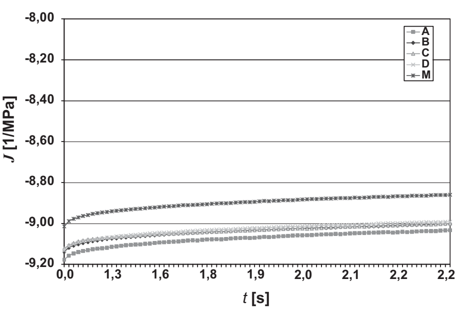


Figure 4.
Creep compliance and master curve

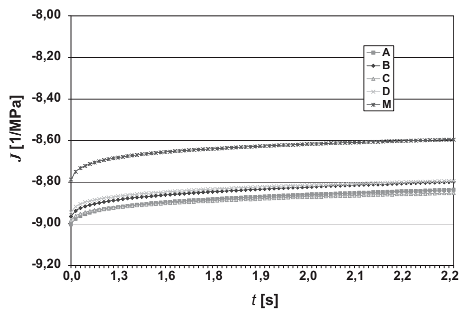
The results of the SIM methods is transformed with the WLF procedure to the master curve (Figure 4) and according to the known equations (**(1)**,**(2)**) is formed compliance master curve.

Material function of creep compliance is presented on the Figure 4[11] and could be otherwise written with following formula:

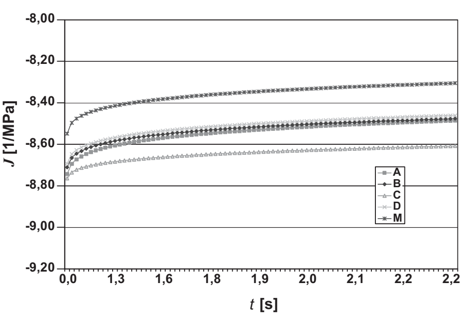
$$J(t) = J_g + J_d \cdot \psi(t) \text{ or } J(t) = J_g + \sum_{i=1}^{i=n} J_d \cdot \left(1 - e^{\frac{t}{\tau}}\right) \quad (3)$$



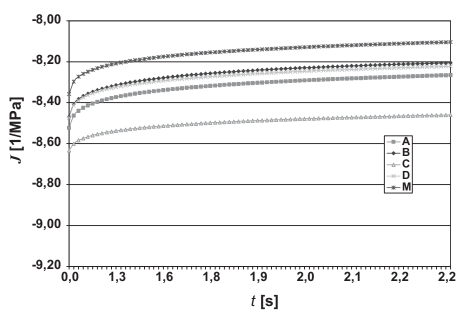
a. Creep curves at 20°C



b. Creep curves at 40°C



c. Creep curves at 60°C



d. Creep curves at 80°C

Figure 5.
Experimental validation of polymer materials applied for polymer tubs.

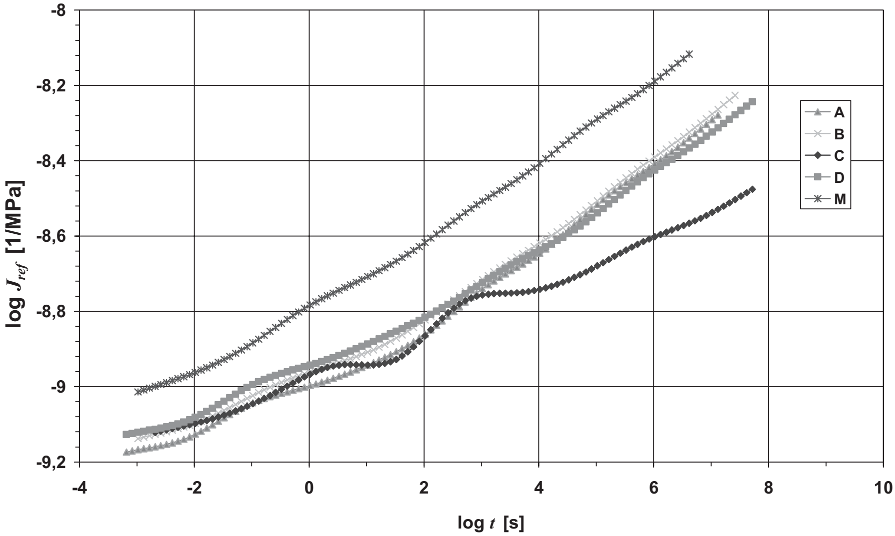


Figure 6.
Master (summary) curve for polymer materials.

where is J_g glassy (instantaneous) compliance and J_e is the equilibrium (retarded) compliance.

Based on practical experience, the optimal experimental window (test duration) should be 4 decades width (10^4 seconds or about 3 hours).

When the master curves are designed, then comparison (benchmarking) criteria are:

- level of initial creep compliance J_g or even equilibrium creep compliance J_e;
- creep time stability (''slope of creep curve'') at given time interval;
- temperature stability of creep properties at given time and given temperatures;

In the real environment, there are always certain combination of creep-recovery as well as relaxation processes, which are very difficult to predict or almost impossible to frame in (mathematical) model.

The product designer has to judge and chose only the phenomenon with the biggest share of impact on the material and consequently product behavior.

Product Durability with Microfillers – Case of Washing Machine Polymer Tub

To validate practical example of product durability has been taken polymer tub (Figure 1) and related polymer material (composite) – $PP + 40\% \times CaCO_3$ from 4 different world's leading washing machine producers. Experimental validation has been conducted in industrial laboratory on commercial available apparatus and according the acknowledged international standard for polymer material testing.[18,21]

The results of experimental validation of all materials from the polymer tubs (A, B, C and D) as well as microfiller (M) for benchmarking are presented on the graphs – Figure 5 and Figure 6.

The master (summary) curve for material properties benchmarking is presented on the graph below – Figure 6.

Conclusion

The advantageous potential of micro fillers is well known and proven approach for

Table 1.
Washing machine tub - traditional and advanced, microfiller composite.

Properties		PP + 20% talcum	PP + 40% $CaCO_3$	Microcomposite
Density	g/cm3	1,04	1,24	0,98
MFR 230/2,16	g/10min	5–20	5–20	20
Tensile E Modulus	MPa	2700	2800	2600
Charpy V-notched +23°C	kJ/m^3	2–3	2–3	3,5
HDT A	°C	65	55	64
Shrinkage Toolbox	%	1,1	1,1	1,2
Gloss	%	−35	−30	−50

material enhancements in industry as well as in the appliance industry.[5,8,22]

In our case it was compared microfiller, which already have advantageous material properties in comparison to the other common PP composites applied for polymer washing tub (PP + 20% talcum, PP + 40% $CaCO_3$) – Table 1.

The low density of microfiler means parts per unit weight of resin and reduced part weight. Consequently, this means cost saving transport, storage and materials handling.[22]

The processing conditions for injection moulding are almost equivalent for the "traditional" PP compounds. Very favorable is also fact, that equivalent shrinkage permits moulding with existing tools as well as lower abrasiveness of microfillers ("more shots" with the same tool).

Besides the aesthetic parts (e.g. filter covers, door frames and control panels) microfillers found application in high stress parts (tubs) as well as other washing machine and dryer parts (e.g. basements, soap dispensers, heat exchanger and pump housings).

The time-dependence of microcomposite and traditional composites (PP+ $CaCO_3$) has shown that there is no substantial difference. This is especially evident at the highest temperatures, where the thermo-mechanical loadings are the highest.

The research has shown, that even the time-dependent properties of PP composites with microfillers are advantageous in comparison to the "traditional" PP composites and could be even more "tailored" for more demanding, advanced applications.

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