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AN ADVANCED HIGH MODULUS (HMG) SHORT GLASS–FIBER REINFORCED NYLON 6: *PART I – ROLE AND KINETIC OF FIBER-GLASS REINFORCEMENTS*

Abstract

Resent developments were oriented on two high-flow, high-modulus grades fiber-glass reinforced nylon 6 (HMG series) grades for autos and other industrial applications requiring high stiffness and high strength. These materials combined the following improved technological (injection molding, vibration welding, etc.) and mechanical performance properties such as greater dimensional stability, higher short-term (strength and stiffness) and long-term (fatigue and creep).

The current and possible applications of these plastics includes auto mirror housing brackets, clutch pedals, clutch master cylinders, ski bindings, steering wheels, levers, auto seat frames, door handles and door lock mechanisms.

In Part I of this paper, we are presenting results of reinforcement analysis with the influence of level of loading and geometrical parameters of used fiber-glass.

Introduction

When selecting existing or developing a new plastic product for specific applications, materials developers and designers dealing with a variety of fiber-reinforcements and resin systems. Knowledge of used materials properties is the first requirement for designing a safe and durable product. A well designed component that employed the right material and process to meet the application end-use requirements. Basically, fiber reinforcements provide desired mechanical, physical and chemical properties. Comprehensive data and practical recommendations on various additives for nylon based thermoplastics are widely presented in [1-3].

The special requirements of the industrial arena, including auto market, appliances, etc. are influencing development of new types nylon (polyamides) based plastics, particularly high-flow grades that retain their high strength and stiffness (Young's modulus).

High modulus/strength fiber-glass reinforced (with 45 – 65 wt. % GF) nylon (polyamides) are emerging in automotive structural body panels, levers, internal and external mirror housings, seat frames, steering wheels, and various heavily stressed door handles.

This family of fiber-glass reinforced or reinforced and filled plastics [1-2] can be considered, that all compositions have the following advantages for highly stressed various solid and hollow parts:

- Good mechanical performance of the injection molded structural parts after several re-molding/re-grind cycles (property losses are minimal).
- Moldability to close tolerances.
- Fast overall processing cycles and ejectability (part release from molding tool) are very good.
- Predictable mold and annealing shrinkage. Small tendency for warpage.
- High flow and toughness in thin sections, easy to fill of complicated shapes of hollow parts.
- Sufficient knit line strength.
- Sufficient weld strength (at various welding technologies, such as vibration, orbital, etc.).

While many development and research programs were oriented on the development on highly fiber-glass reinforced long-fibers nylon based plastics, a few studies concentrated on:

- High modulus materials development with improved viscosity close to that of standard unfilled nylon.
- Selection of high modulus (HMG) nylon 6 based plastics for optimized design and advanced processing technology.

Reinforcement of High Modulus (HMG) Nylon: Process Analysis and Results

Fiber-glass is added to polymer (matrix) when it is necessary to improve (or reach needed parameters) their mechanical properties. The reinforcing fiber-glasses may be short and long. Standard fiber-glasses are cylindrical, but it is possible to change a shape of the cross-section to oval, tri-lobular, etc. A practical guideline for maximum loading of short fiber-glass is 50 vol.%[1]. In nylon based

[1] vol.% - level of reinforcement or filled by volume. Some authors are using the term "packing fraction" for this parameter.

thermoplastics, the 50 vol.% fiber-glass loading corresponds to approximately 70 wt.% as a maximum loading of reinforcement, due to limitations of standard compounding techniques. Nylon powder coatings may use a multiplicity of particulate fillers (melt compounded) at high filler level up to 60 vol%.

The following key reinforcement (by fiber-glasses) variables (parameters) are more influential on mechanical properties of thermoplastics:

- Fiber-glass diameter - d_f.
- Average fiber-glass length - $L_{average}$.
- Aspect ratio r_f (at any phases of manufacturing, when the average fiber-glass length may be changed)
  $$r_{f,average} = \frac{L_{f,average}}{d_f}.$$
- Fiber-glass content (vol.% or wt.%).
- Fiber-glass surface state.
- Fiber-glass mechanical performance (tensile strength - σ_f and tensile modulus - E_f).
- Coupling to the matrix (base resin).
- Fiber-glass orientation and distribution (through thickness) in highly loaded/stressed areas of injection molded part[2].

Enhanced mechanical performance (tensile or flexural strength, rigidity/stiffness and fracture toughness) of fiber-glasss reinforced thermoplastics is dependent on optimum fiber-matrix interface design coupled to minimum attrition of glass filament length during a sequence of process steps. Inter-phase design is identified as the central gem affecting short fiber-glass thermoplastics mechanical properties over the service lifetime of an injection molded part [3]. It should be realized that it is quite difficult to mix fibers with polymer (matrix) during compounding and injection molding because of the exceptionally high viscosity of most polymers, even at elevated temperatures.

During the manufacturing process (compounding, injection molding, etc.) fibers are involved in a lot of interaction with machinery. As a result, fibers length may be reduced dramatically. In order to minimize short fiber-glass damage (during processing) and maximize thermoplastic mechanical performance we need to optimize all phases of the manufacturing cycle (the compounding and injection molding). The fiber-glasses for composites (thermoplastics and thermosets) are manufactured in the range of 8 μm to 25 μm. The diameter d_f of fiber-glass for nylon based plastics is generally 9-10 μm (but may vary). Some researcher observed an increase of tensile strength of GF reinforced nylon 66 for this diameter compared with 13 μm. Fiber-glass types, having a 13-14 μm diameter, are generally designed for PP based plastics. However, both tensile strength and fracture toughness for short fiber-glass reinforced polypropylene (PP) are improved by using the much smaller 9-10 μm diameter fiber [2, 4]. Conversely, there is information that tensile and flexural strength are adversely affected by 17 μm size fibers.

A wide evaluation of the influence of fiber-glass reinforcements on mechanical performance of injection molded nylon 6,6 (30 wt.% GF) is presented in [5]. The fibers with nominal diameters of 10, 11, 14 and 17 μm were used for this analysis (Tables 1-2). Nominal mechanical properties of used E and S-2 fiber-glass are shown in Table 6. The presented results show that the elastic properties of short fiber-glass reinforced nylon 6,6 (30 wt.% GF) are not strongly affected by the fiber-glass diameter in the 10 – 17 μm range. Elongation at break, tensile and flexural strength, and un-notched impact (Izod) all decreased by 5~10% over the 10 – 17 μm diameter range. Notched impact (Izod) showed a small increase over the same range. An addition of 20 wt.% of S-2 fiber-glass to the 17 μm E-glass resulted in a 8% improvement of the strength. Note: The tensile strength of combined fiber-glass composition by the fiber diameters ("E17"/"S2S") is less than the tensile strength for "E11"fibers (182 MPa with 174 MPa).

A special study was conducted on the influence of a fiber-glass (with diameter 10 μm and 13 μm) on mechanical performance of glass reinforced (GF) and impact modified (IM) nylon 6 based plastics with the following compositions (Table 3):

- 25 wt.% GF + and 10 wt.% IM.
- 35 wt.% GF + 5 wt.% IM.

This study shows an increase of the tensile and flexural strength for the fiber 13 μm diameter compared with 10 μm fiber diameter. Increase of mechanical performance for the fiber 13 μm diameter compared with 10 μm fiber diameter is as follow:

- For tensile strength: ~8 - 20%.
- For flexural strength: ~19 - 40%.

These results are at variance with the data achieved for nylon 66 [5] and PP [1] based plastics and should be re-checked in the future. Due to observed discrepancies in published [1, 3, 5] and discussed above

[2] Skin-core effects are very important for the parameters of flexural strength and stiffness, when stress-strain distribution through thickness isn't uniform.

results on the influence of the diameter d_f on mechanical performance of nylon, we initiated additional investigation for highly reinforced (GF ≥ 50 wt.%) nylon based thermoplastics (both HMG series). For this investigation we used fiber-glasses with the following sizes (diameters d_f, in μm) of the fibers: 10; 13 and 16. Tables 4-5 shows the reinforcements effects for two nylon 6 based plastics HMG series with 50 wt.% GF and 63 wt.% correspondingly. The tensile and flexural strength decreases by ≈ 18 – 20% when diameter d_f increases from 10 μm to 16 μm. Notched impact data wasn't sensitive to the influence of d_f for both plastics. As the results of this investigation, for composition of HMG plastics we used fiber-glasses with diameter equal 10 μm.

After a sequence of compounding and injection molding processes, the fiber-glass length is reduced from 3-5 mm to less than 0.45 mm for an average ($L_{average}$) depending on cumulative fiber-glass damage. This process highly dependent on fiber-glass content (vol.% or wt.%). Some of this is very interesting and helpful for the analysis result, which were presented in [1, 3-4]. The fiber-glass length (an average) $L_{average}$ is calculated by the following equation:

where:

$$L_{average} = k(t)\frac{d_f}{v_f}, \quad (1)$$

v_f - Fiber volume fraction (or in %).

$k(t)$ - Parameter (constant).

Shear loading forces act on the brittle fiber ends to cause a certain amount of fracture depending on v_f. This mechanical behavior limits the effective length $L_{effectivre}$ of fiber-glass to a minimum amount dictated this relationship. At low levels of fiber-glass loading (0-6 wt.%), the stress concentration at fiber-glass ends is quite high. The inherent brittleness is due to the relatively small fiber-glass diameter d_f. With little overlapping of the stress fields around fiber-glass in dilute medium, the notched Izod values are quite small. At higher loading of fiber-glass, the thermoplastics become more ductile and exhibit corresponding increased notched impact values. By decreasing the mean fiber end spacing below a critical threshold value (six times the fiber diameter), the stress fields around individual fibers overlap strongly to modify the deformation characteristics of the polymer matrix. Therefore, a matrix toughening mechanism results from plasticity around fiber-glasses.

It is possible to predict the tensile strength σ_c of injection molded fiber-glass reinforced nylon based thermoplastics by the following equation:

$$\sigma_c = \frac{v_f \sigma_f}{(1 - L_c / 2L_{average})C_o(t, RH)} + v_m \sigma_m(t), \quad (2)$$

where:

- $\sigma_m(t)$ is strength at yield of polymer (matrix) at temperature *t* (°C), in MPa.
- $C_o(t, RH)$ - is the orientation factor with the influence of temperature *t* and moisture (*RH, %*) effects.
  Value of $C_o(t, RH)$ is in the following range:
  $$1 \ge C_0(t, RH) \ge 0.3.$$
  The orientation parameter $C_o(t, RH)$ is equal to 1 for longitudinal (at flow direction) orientation. The tensile strength at this direction reaches *maximum* value. For perpendicular to flow direction, this value may decrease by 30% - 50% (approximately) from the plastic strength at flow direction (at test temperature *t* and moisture in plastic). The orientation of any single fiber may be calculated from its elliptical profile by the following equation:
  $$\cos(\vartheta) = \frac{d_{minor}}{d_{major}} = \frac{4A_{ellipse}}{d_{major}}, \quad (4)$$
  where: ϑ - is the angle the fiber-glass axis makes with the melt-flow direction: d_{minor} - is the minor axis, $d_{minor} = d_f$; d_{major} - is the ellipse major axis, and A - is the area of the ellipse. The $\cos(\vartheta)$ data is the key factor in calculation of the value of orientation factor/parameter $C_o(t, RH)$. The details on methods of $C_o(t, RH)$ calculation with the influence of Weibull distribution of strength are presented in [7].
- L_c - is critical fiber length, in mm or in μm.
  The critical fiber length L_c may be determinate by the following equation:
  $$L_c = \frac{d_f \sigma_f(t)}{2\tau(t, RH)}, \quad (3)$$
  where: $\tau(t, RH)$ - is the interfacial strength of polymer (matrix) with the influence of temperature *t* and moisture *(RH)* effects. The fiber length L

distribution is a function $f(L)$ that may be determinate by the following equation (if $L \rhd 0$) :

$$f(L) = abL^{b-1}\exp(-aL^{b}), \qquad (4)$$

where: a and b are scale and shape parameters respectively. The details on the estimation of average fiber-glass distribution are described in [8].

- $\sigma_f(t)$ - is effective fiber-glass strength , in MPa.

  The effective value of fiber-glass strength $\sigma_f(t)$ is equal (approximately) to half of the strength of continuous fiber-glass (Table 6). For continuos fiber-glasses the value of σ_f varied from 3.4 GPa (for E-type fiber-glass) to 5.9 GPa (for silica fibers).

Discussion

The short fiber-glass length and diameters were evaluated by image analysis and optical microscopy on fiber-glass samples extracted from the injection molded multipurpose ISO specimens after high-temperature ashing. Measurements of fiber-glass orientation parameter $C_o(t, RH)$ was performed on the cross-sections of a these multi-purpose ISO specimens machined perpendicular to the melt-flow direction.

The trends in mechanical properties of the short fiber-glass reinforced nylon are as follow (Table 7):

- Tensile strength versus fiber-glass content is linear (in fiber-glass reinforcement range from 6 wt.% to 40-45 wt.% GF).
- Impact behavior increases with increased fiber-glass interaction due to higher v_f - vol.% (or wt%).
- There is a decrease in fiber-glass length from 4.7 mm to 0.4-0.2 mm (400-200 μm).
- The average of fiber-glass length is inversely related to fiber-glass loading (by volume or weight).

At elevated temperature conditions, the influence of reinforcement is a more critical factor than at room temperature, due to possible changes in mechanical and viscoelastic properties of polymer (matrix). For high levels of reinforcements (GF ≥ 50 wt.%) the critical aspect ratio $(\frac{L_c}{d_f})$ is approximately 20:1. At a range of 20 wt.% ~ 30 wt.%, the levels of reinforcement ratio is 35 (28):1 (Table 7). Based on theoretical assumption presented in [1 and 6], the strengthening effects of fiber-glass reinforcement will increase with aspect ratio $(\frac{L_c}{d_f})$ asymptotically is reaching a limit close of 400:1. This ratio is more typical for highly loaded long-fibers reinforcement conditions. The results presented in Table 7 are in disagreement with these assumptions, because for high levels of reinforcements (GF ≥ 50 wt.%) an increase of mechanical performance was achieved at lowest levels of the aspect ratio.

Concluding Remarks

The average of fiber-glass length is inversely related to fiber-glass loading (by volume or weight). For high levels of reinforcements (GF ≥ 50 wt.%) the critical aspect ratio $(\frac{L_c}{d_f})$ is approximately 20:1.

The tensile strength of injection molded nylon 6, increases linearly with the fiber-glass content up to 40 - 45 wt.%. Following the increase of fiber-glass content of 45 – 50 wt.%, the tensile strength then asymptotically is reaching a limit of *maximum* in the mechanical performance and *maximum* (63-67 wt.%) in loading (packing) of fiber-glass reinforcements.

Impact behavior increases with increased fiber-glass interaction due to higher v_f - vol.% (or wt%).

At elevated temperature conditions, the influence of reinforcement is a more critical factor than at room temperature, due to possible changes in mechanical and viscoelastic properties of polymer (matrix).

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Table 1. Influence of the Short Fiber-Glass Diameter d_f (E-glass) on Mechanical Performance of Fiber-Glass Reinforced Nylon 6,6 Based Plastics (30 wt.% GF).

Diameter of GF (in μm)	***E10***	***E11***	***E14***	***E17***
Tensile Strength, MPa	184	183	174	164
Tensile Modulus, GPa	9.73	9.76	9.55	9.50
Tensile Strains, %	2.83	2.80	2.70	2.49
Flexural Strength, MPa	287	285	270	249
Flexural Modulus, GPa	9.20	9.21	9.29	9.01
Un-notched Impact, J/m	979	894	775	568
Notched Impact, J/m	130	130	135	139

Table 2. Influence of the Short Fiber-Glass Diameter d_f (E-glass) on Mechanical Performance of Fiber-Glass Reinforced Nylon 6,6 Based Plastics (30 wt.% GF).

Diameter of Short Fiber-Glass - d_f, μm	$\frac{E17}{S2S}$	$\frac{E17}{S2S}$	$\frac{E17}{S2L}$
GF Composition ratio, %	95/5	80/20	80/20
Tensile Strength, MPa	164	173	174
Tensile Modulus, GPa	9.43	9.66	9.73
Tensile Strains, %	2.54	2.75	2.66
Flexural Strength, MPa	250	261	261
Flexural Modulus, GPa	8.75	9.14	8.69
Un-notched Impact, J/m	628	805	724
Notched Impact, J/m	136	134	137

Table 3. Influence of the Fiber Diameter d_f on Mechanical Performance of Short Fiber-Glass Reinforced/Impact Modified Nylon 6 Based Plastics

Fiber-Glass Content, wt. %	**25**	**25**	**35**	**35**
Impact Modifiers, wt.%	10	10	5	5
Fiber diameter, μm	10	13	10	13
Tensile Strength, MPa	112	121	125	145
Flexural Strength, MPa	167	199	181	254

Table 4. Influence of the Short Fiber-Glass Diameter d_f on Mechanical Performance of High Modulus (HMG) Fiber-Glass Reinforced Nylon 6 Based Plastics (50 wt.% GF)

Diam. of Fiber-Glass- d_f, μm	**10**	**13**	**16**
Tensile Strength, MPa	224	203	197
Flexural Strength, MPa	337	313	301
Flexural Modulus, GPa	14.0	13.5	13.6
Un-notched Impact, J/m	1240	1016	947
Notched Impact,	133	121	129

Table 5. Influence of the Short Fiber-Glass Diameter d_f on Mechanical Performance of High Modulus (HMG) Fiber-Glass Reinforced Nylon 6 Based Plastics (63 wt.% GF)

Diam. of Fiber-Glass- d_f, μm	**10**	**13**	**16**
Tensile Strength, MPa	248	232	223
Flexural Strength, MPa	407	346	337
Flexural Modulus, GPa	19.1	17.7	18.0
Un-notched Impact, J/m	1230	1069	1016
Notched Impact, J/m	139	139	134

Table 6. Mechanical Properties of High Modulus Fiber-Glasses

Material	**Tensile Strength, MPa**	**Tensile Modulus, GPa**	**Specific Gravity**
"A" fiber-glass	2.400	67	2.50
"C" fiber-glass	2.750	69	2.49
"D" fiber-glass	2.400	52	2.16
"E" fiber-glass	3.400	72	2.55
"ECR" fiber-glass	3.620	73	2.62
"R" fiber-glass	4.400	86	2.55
"S &S2" fiber-glass	4.820	87	2.49
Silica fibers	5.900	72	2.20
Hollow E-glass	1.400	50	2.00

Table 7. Influence of the Short Fiber-Glass Reinforcement on Fiber Length in Molded Thermoplastic

GF wt %	**GF vol. %**	**Fiber Length μm**	***Constant*** k	**Tensile Strength Mpa**
0	0	0	0	82
10	0.048	436	0.216	104
20	0.101	337	0.351	140
30	0.181	261	0.457	177
45	0.230	225	0.422	198
50-HM	0.309	201	0.663	262
63-HM	0.44	188	0.768	280

Key Words

Nylon, reinforcement, fiber-glass, performance.

BASF Corporation
3000 Continental Drive - North
Mount Olive, New Jersey 07828-1234

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