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FORWARD TO BETTER UNDERSTANDING OF OPTICAL CHARACTERIZATION AND DEVELOPMENT OF COLORED POLYAMIDES FOR THE INFRA-RED/LASER WELDING: *PART I – EFFICIENCY OF POLYAMIDES FOR INFRA-RED WELDING*

Abstract

The influence of a wide range of the infrared (IR) wavelengths (from 830 to 1,064 nm) on the optical properties of welded thermoplastics was evaluated for unfilled, filled and reinforced polyamide 6, 66 and amorphous grades. Presented results and developed recommendations will help, designers, technologists and materials scientists in welded parts design, materials selection and new materials development for various laser welding (LW) applications.

Introduction

Infrared/laser through-transmission welding (TTLW) is an innovative method of joining technology for various thermoplastics. While many development and research programs were oriented towards optimization of mechanical performance of the weld and evaluation of absorption characteristics [1, 5-6], only a few studies [2-3, 7-8] concentrated on:

- Characterization of transmittance and absorption of colored polymers and plastics;
- Development of colored plastic grades for infrared/laser welding (LW) applications.

This study describes a comprehensive, optical characterization of colored and non-colored, polyamides (PA), focussing on the influence of plastic composition, pigment type, and joint design issues. The results of the optical characterization and the presented recommendations will contribute to a better understanding of IR welding process, plastic selection, materials development, and welding equipment design for successful industrial applications.

Basic Principles for LW of Thermoplastics

In polymer welding we need to heat and melt the polymer at the joined surfaces for weld inter-phase formation. For LW technology, two approaches have been applied to heating the surfaces to be joined leading to localized thermoplastic(s) melting and subsequent welding of the parts:

- Non-contact laser welding (NCLW).
- Through-transmission laser welding (TTLW).

By heat generation, melt layers and inter-phase formation, LW methods may be classified into the following groups:

- Scanning (moving) of the laser beam along the weld contour [1-5];
- Simultaneous heat generation by the family of laser beams, delivered by fiber-optic at the contour of the weld [6,9].

Analysis of the differences of these LW methods is very important for clear understanding of the requirements for material(s) selection and parts design.

Non-Contact Laser Welding (NCLW)

NCLW is typically used for joining rigid thermoplastics. The process of NCLW, preferably using butt joints is very similar to non-contact or contact hot plate welding (HP). For HP joining technology, the parts to be welded are brought into contact after heating and melting. Welding of plastic parts results from localized melting of the material(s) and the pressure-induced flow of material, which causes diffusion and interlocking at the weld inter-phase area. Different physical mechanisms (such as *radiation, conduction, convection and subsequent contacting*) are used to generate localized melting of layers of material(s) for NCLW. The parts selected for welding material(s) should provide energy absorption and melting at localized areas for inter-phase formation. Optical data on laser energy absorption and reflection is very helpful for this LW method.

Through–Transmission Laser Welding (TTLW)

TTLW may be used to join colored plastics with a broader range of design combinations than NCLW:

- Rigid to rigid (molded, extruded, etc.).
- Flexible to rigid (films and soft TPE to molded).
- Flexible to flexible (films, soft TPE, etc.).

In LTTW the plastic parts to be joined are brought into direct contact prior to welding (Figure 1). The welding process requires two plastic materials, which transmit the laser energy (LE) to different degrees. The optically transparent (at the laser wavelength) part (**A**, such as natural, or colored with non-absorbing pigment) is in contact with an optically dense part (**B**, typically carbon black filled, or colored with absorbing pigment). The laser beam is transmitted through part **A** with minimal losses and totally absorbed within the surface (interfacial) layer of part **B**. Direct contact between the parts ensures heating of part **A** at the joint interface. Welding occurs upon melting and fusion of both materials (**A** and **B**) at the interface. The heating and melting of the polymer is initiated by absorption of energy in part **B**. The heat from this area(s) is transferring to the surface of the laser energy transmissible part **A**. Both melt layers (**A** and **B**) create the weld inter-phase.

For TTLW, it is critically important to achieve a sufficient and consistent heating of the plastic in the region of the join during pre-melt and fusion phases. This condition will produce consistent thickness for the weld inter-phase and the desired mechanical performance of the weld. The specifics of the weld formation between parts **A** and **B** should be taken into account in colored material selection and joint design. Optical data on LE transmission and absorption is very helpful for selecting materials **A** and **B** in this LW method.

Advantages of TTLW Technology

Previously we discussed and illustrated [3] the following basic advantages of TTLW technology:

- Accurate, non-contact, heat transfer with the possibility of optimizing the welding temperatures.
- Improved localization of the heat affected zone, by varying the shape and size of the laser beam, and control of melt flash in the join area.
- No visible damage or marking on the external colored surfaces correlated to the joint area.
- Welding of pre-assembled plastic components.
- Design freedom. Minimal limitations on the geometry and the size of the plastic parts to be joined.
- Easy to automate, short welding cycle time. Rapid welding speeds permitting welding of long and wide thermoplastic parts with acceptable weld times.
- Absence of vibration of the parts in the welding process (in contrast to ultrasonic and linear welding technologies) that permits welding of sensitive electronic and medical components.
- High mechanical performance of welded joints for various PA compositions (unfilled and fiberglass reinforced, and colored/pigmented).

Process Limitations

Unfortunately, TTLW technology has the following limitations, which may be reduced by proper selection of material and welding method:

- Material dependence:
  - TTLW process requires different LE absorption characteristics for thermoplastic parts **A** and **B.**
  - Poor response to some additives (fillers, impact modifiers and pigments).
- Intimate contact required at joint (future weld) area.
- Possible development of the residual stresses at the weld inter-phase for highly rigid plastics.

Optical Properties of Polyamides (PA) at Near-Infrared Wavelengths

Specifics of LW Technology and Key Properties Needed for Thermoplastic Selection and Design

Optimized design for LW requires knowledge of the key optical properties of plastics including the effects of material composition, color version, processing technology and end-use conditions (time, temperature, moisture, ultraviolet exposure, etc.). As we discussed previously, the basic properties of the polymer (matrix) and various additives affect what happens to the infra-red/laser energy absorption, reflection and transmission, and finally to the mechanical performance of the weld. For LW of thermoplastics the following three properties/parameters are very important for modeling and understanding the LW process:

1. ***Plastic(s) composition and material state***
   - Plastic(s) composition (fiberglass or fiber-carbon, etc.) reinforcement, mineral fillers, etc.
   - Additive(s) particle shape and sizes.
   - Color/pigments/dyes (type and content)
   - Material state in joined parts/specimens before LW (dry as molded, moisture content).

2. ***Physical properties (polymer and additives)***
   - Polymer melt point (T_m).
   - Plastic(s) density.
   - Heat capacity and thermal conductivity.
   - Type of microstructure (crystallinity parameters CI, CSP, etc.).

3. ***Optical properties***
   - LE transmission and LE absorption.

- Polymer and additive refractive indices.

Table 1 compares specific values (or ranges, as appropriate) of some of these properties for several PA (6, 66, amorphous) and for one optical polymer (PC). The present study focuses on the optical characterization of colored PA 6 based thermoplastics, including the influence of pigments/dyes, and reinforcements/additives. Only limited data on the relevant optical properties of colored nylon is available in published articles and reports [2, 8, and 10].

Test and Evaluation Methods

The efficiency of LW methods (NCLW and TTLW) *is strongly dependent on the optical properties of the plastic parts to be joined* and the laser specifications. In some cases *we need to take into account additional optical properties of the third substance*, which is placed at the area of heat generation between the joined surfaces.

To better understanding the optical properties of PA at IR wavelengths that are important for welding process, we will discuss the methods of evaluation and basic optical properties of various thermoplastics including PA. Optical testing and evaluation (OTE) of plastics for LW technology has some similarities to characterization of "optical polymers" and various optical components. At the current time no standard methodology or uniform specimens exist for OTE of polymers and plastics for LW applications. In this study we used test and evaluation procedures [3] similar to ASTM standards[1] for optical polymers.

The *LE transmittance* (*T*, in %) is given by:

$$T = 100\frac{I_t}{I_0},$$

where I_0 is the laser beam intensity incident on the specimen and I_t is the laser beam intensity passing through the specimen.

The *LE reflectance* (*R*, in %) is equal to:

$$R = 100\frac{I_r}{I_0},$$

where I_r is the intensity of the reflected laser beam. The reflectance as measured has two contributions – specular (from the front and rear surfaces of the specimen) and diffuse (from irregular surfaces and within the bulk of the specimen). For optically clear polymers only specular reflection is significant and the reflectance can be calculated from the reflection loss.

The reflection loss (R_l, in %) is calculated by:

$$R_l = 100\frac{(n-m)^2}{(n+m)^2},$$

where ***n*** and ***m*** are the indexes of refraction of the two media involved (***n*** – thermoplastic, ***m*** – air). Using the refractive index data in Table 1 the reflection losses for PA 6 (or PA 66) are ≈ 4.5% per surface. This number decreases with increasing wavelength and temperature.

The *LE absorption* (*A*, in %) is equal to:

$$A = 100\frac{I_0 - I_t - I_r}{I_0}.$$

When the absorption is small (A < 10%), this can be approximated to $A = 100 - T - R$.

The *LE absorption coefficient* is equal to:

$$A_c = \frac{1}{t}\ln\frac{I_t}{I_0},$$

where t is the thickness of the thermoplastic specimen.

In addition to three key optical properties (*transmission, absorption, refractive index*) that are important for LW the following five optical properties (*clarity, haze, birefringence, yellowness and color*) are used to characterize plastics and films in the design of various optical components. Results of testing [12-13] at visible wavelengths shows that most of semi-crystalline PA are nearly opaque above 2.5 mm, transparent below 0.5 mm and translucent at intermediate thickness.

Some of the published results show that the following additives may dramatically reduce light transmission of PA: carbon black, pigments, fillers, reinforcements and foaming agents. Light transmission of semi-crystalline plastics can be reduced also by the increasing the crystallinity and the number of spherulites. Reducing the crystallization rate and spherulitic microstructure may increase transparency of PA.

The *maximum transmission* of visible light for optical polymers of any thickness is as follow [12-13]:

- Un-coated acrylic ~ 92%
- Un-coated PC (or PS) ~ (89 – 90)%.

Here the reduction in transmission from 100% is essentially due to specular reflection losses from the surfaces with minimal or no diffuse reflection losses. Similarly, unfilled amorphous PA has the highest light transmission among PA ~ 86-90%, with slightly lower values reported [14] for PA 12 (~ 85%).

Materials, Specimens and Color Versions

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[1] ASTM D-1003, ASTM E-166, ASTM D-1925, ASTM D-542.

In this study we used three types of commercially available PA: 6, 66 and amorphous. The following grades and color versions were evaluated in this study:

- Non-reinforced/non-filled plastics
  - PA 6 (*various colors including carbon black and non-carbon black*)
  - PA 66 (*natural state only*)
  - Blends of transparent, amorphous PA with PA 6 (three versions with amorphous PA content, by weight: 0, 30 and 40 wt.%).
- Short fiber-glass reinforced plastics
  - PA 6 based, with the level of reinforcement from 6 wt.% to 63 wt.% GF (*natural state, carbon black and non-carbon black)*
  - PA 66, with the level of reinforcement from 15 wt.% to 45 wt.% GF (*natural state only).*

Standard injection molded ASTM/ISO multipurpose specimens and rectangular plaques were used for the optical characterization of the evaluated thermoplastics. Sizes (length x width) of molded plaques are 150 mm by 100 mm (approximately) at three thickness (1.6, 3.2 and 6.25 mm).

Key Optical Properties of Colored PA 6 Plastics

Absorption of Laser Energy (LE)

At near-infrared spectral wavelengths, the uncolored plastics (color version – natural state) absorb a very small portion of LE, because only overtone- or combination-vibrations are stimulated. Experimental data on the absorption characteristics of five colored, PA 6, materials over a wide wavelength range (from 600 to 1500 nm) was discussed in [10]. Over the near-infrared range of interest for diode and Nd:YAG lasers (from 800 to 1100 nm) a *maximum* of 20% of the laser energy was absorbed by uncolored (natural state) PA (Figure 2). The additives and colorant (pigments/dyes) may control the absorption properties of the various PA. For example some “Organic green” colorants can increase absorption of nylon 6 to 60~90%, depending on wavelength.

Highly transmittable optical polymers (color version - natural state) are not sensitive to wavelength changes in the range from 400 to 1080 nm (Figure 3). The transmittance minima at approximately 1200, 1400 and 1700 nm represent overtone and combination absorption bands of the polymer. Many uncolored (natural state) plastics have a yellow or straw color (with a measurable yellowness index). This can be seen as a failing-off in the blue area of the light transmission behavior at wavelength ≈ 400 nm (Figure 3). A blue toner is added to the polymer to make it appear “as water clear”. Both the types of colorants (pigments/dyes) and the concentration (wt.%) of the colorants play a very important role in the optical properties at near-infrared wavelengths.

According to [10] GF reinforcement affects absorption significantly, increasing the absorption by 2.3 times for reinforcement range from 15 to 50 wt.% GF (Figure 4). At the same time, for 50 wt.% GF PA 6 an increase was observed in *LE reflection* from 12% to 31% [10], suggesting the transmittance has decreased 2-3 times. Both factors (*LE absorption and LE reflection*) *will affect LE transmittance.*

Transmittance of Laser Energy (LE)

In general, for short GF reinforced, PA 6 (with fiber length ≈ 180 - 320 μm and fiber diameter ≈ 10 –13 μm), the transmission decreases monotonically with increasing short GF content from 0 to 63 wt. % (Figure 5). We have argued that the decrease in transmission is due primarily to increased light scattering [3]. This can be seen in Figure 5, which shows an increase in effective pathlength {PA absorbance (at 1.39 μm), normalized to PA content (wt. %)} as the GF content increases from 0 to 63 wt. %. If the normalization to GF content is removed we see that the observed pathlength through the PA component is approximately constant over this composition range. The intrinsic absorption (over all wavelengths in the near infrared region) will remain virtually unchanged. Any apparent increase in observed absorption is a result of diffuse scattering. It is this effect that primarily determines the LE transmittance.

Blending PA 6 with amorphous PA (Figure 6) has a beneficial effect on LE transmittance. Increasing the amorphous phase in these blends to 40% yields about 90% transmittance, the same as for pure amorphous nylon. This is very close to the theoretical value, limited only by specular reflectance from the specimen surfaces. There is no apparent wavelength dependence, as is the case for optical (PC type) plastics where the transmission was unchanged from 830 to 1,064 nm (see Figure 3).

Except for the green specimen, decreasing the wavelength from 1,064 nm to 830 nm slightly decreases the transmittance of four colored and natural state non-filled PA 6 based plastics (Figure 7). These results contrast some of the previously published data [10, and Figure 2]. PA 66 based plastics are less transmittable (Figures 8-9) when compared to the PA 6 based plastics. These differences are more significant at high levels of reinforcement (GF ≥ 25 wt.%) and will affect the level of energy needed for melt-weld preparation and welding time (at the same LW parameters).

Reflectance of Laser Energy (LE)

The reflectance of LE plays a very important role in material selection for LW technology applications. Unfortunately we did not find published data for PA based plastics showing the influence of thermoplastics structural composition (reinforcements, fillers and impact modifiers), using colorants/dyes (type and concentration) on parameters of LE reflectance or suggestions on material selection. Our current investigation, published results [1, 4] and developed OTE methods were focused on evaluation of LE transmittance (as the parameter of final measurements) and LE absorption. We have been able to infer the critical effects of LE energy reflectance (especially due to diffuse scattering) from our measurements of effective pathlength [3].

Concluding Remarks

Colored polyamides (PA) are high performance semi-crystalline thermoplastics with a number of very attractive mechanical and technological properties for various welded parts. Selection of thermoplastics for infrared/laser welding technology depends on nature of method applied, material structural composition, various additives, color versions of joined PA:

- For non-contact laser welding (NCLW), the selected PA should strongly absorb laser energy and provide heating and material melting at localized areas.
- For laser through-transmission welding (TTLW), the selected PA should have these different properties: one should be through-transmissible; second should strongly absorb laser energy, heating and melting materials at localized areas (inter-phase)
- Selected pigments and dyes (type, content, particle shape and sizes) should possess the appropriate optical properties (either to absorb or to transmit laser energy) needed for the design of LW technology.
- Structural composition (reinforcements, fillers, impact modifiers, etc.), additives used (such as processing aids, heat stabilizers, fire retardant, etc) should be taken into account in the material pre-selection phase.

Results from this report will help designers, technologists and material developers, in selection of PA based plastics for LW technology, the design of welded parts and technology optimization.

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Key Words

Laser welding, polyamide, optical characterization.

Table 1. Refractive Index and Density of Nylon (PA) And Polycarbonate PC (Optical Polymer). Color Version: Natural State.

Type of PA	**Density, g/cm^3**	**Refractive Index**
PA 6	1.13	1.538
PA 66	1.14	1.544
Amorphous PA	1.13	1.562

PC	1.20	1.586

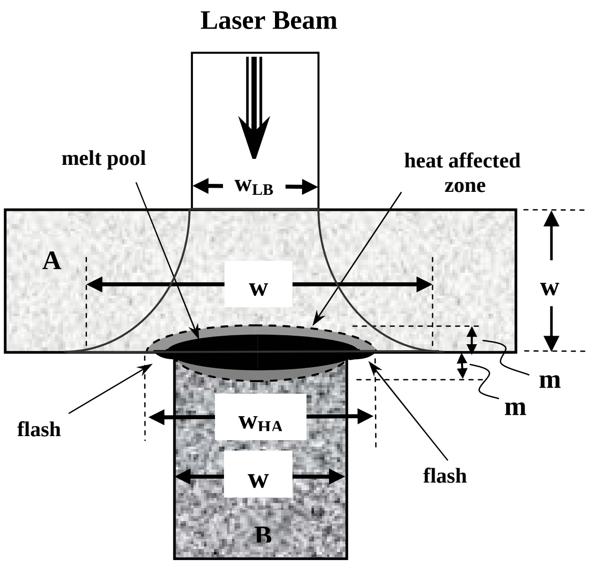

Figure 1. Principles of the formation of the melt pool within the heat affected zone for TTLW. Legend: **A** is a thermoplastic having variable transmission/scattering; **B** is thermoplastic that absorbs the transmitted light at the interfacial region; $\mathbf{W_{HAZ}}$ = width of heat affected zone; $\mathbf{W_B}$ = width of part **B**; $\mathbf{W_L}$ = width of laser beam at joint; $\mathbf{W_{LB}}$ = width of laser beam at face of part **A**; $\mathbf{m_A}$ = depth of heat affected zone, part **A**; $\mathbf{m_B}$ = depth of heat affected zone, part **B.**

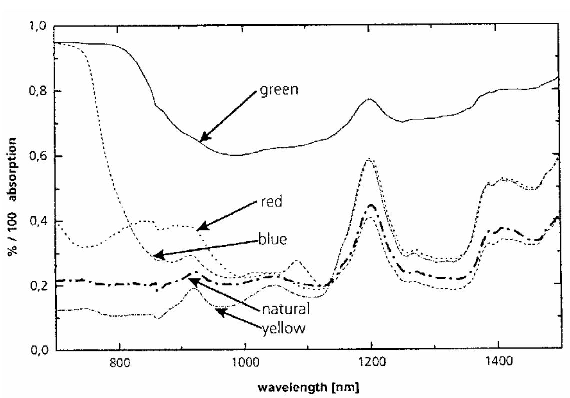

Figure 2. Influence of wavelength on absorption (*A*) properties for the following versions of colored PA: green, red, blue, natural and yellow.

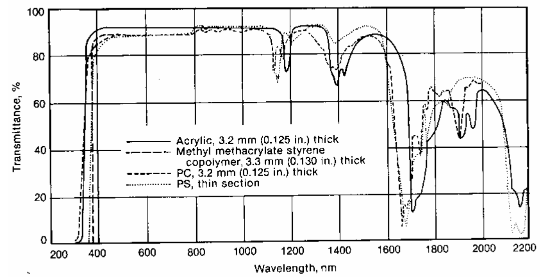

Figure 3. Influence of wavelength on transmittance (*T*) for four optical plastics.

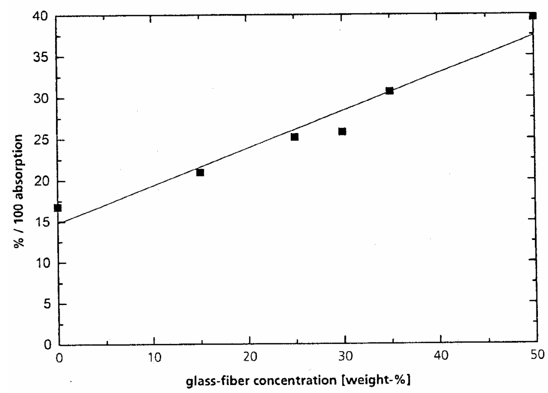

Figure 4. Absorption properties (*A*) of PA with the influence of fiberglass reinforcement (0-50 wt.% GF).

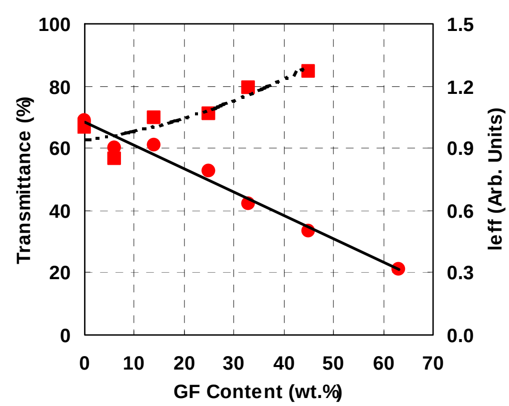

Figure 5. Transmittance (*T*) at 1,064 nm and effective pathlength (l_{eff},) of PA 6 plastics with the influence of fiberglass (GF) content (wt. %). Effective pathlength (l_{eff}, normalized to 1.0 at 0% GF content).

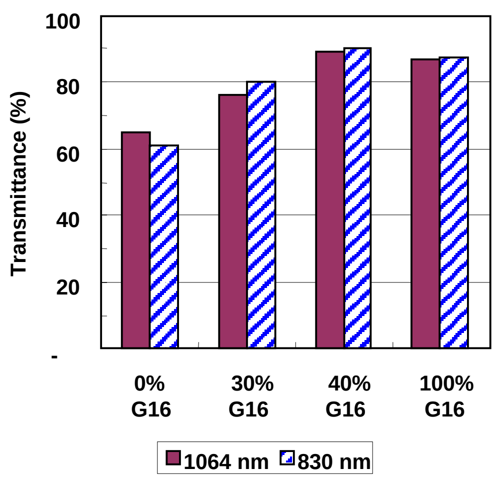

Figure 6. Influence of wavelength (at 1,064 and 830 nm) on transmittance (*T*) properties for the blends of PA 6 with amorphous PA (G 16).

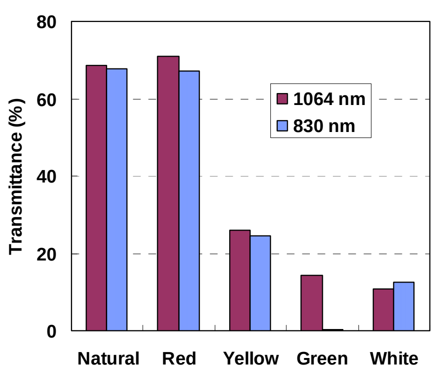

Figure 7. Influence of wavelength (at 830 and 1,064 nm) on transmittance (*T*) properties for the following versions of colored PA: red, yellow, green, white and natural. Thickness of the specimens is 3.2 mm.

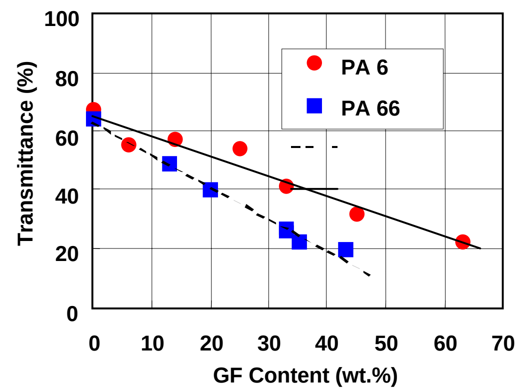

Figure 8. Transmittance of PA 6 vs. 66 based plastics with the influence of fiberglass reinforcement (at wave length 1,064 nm). Thickness of the specimens is 3.2mm. Color version: natural state.

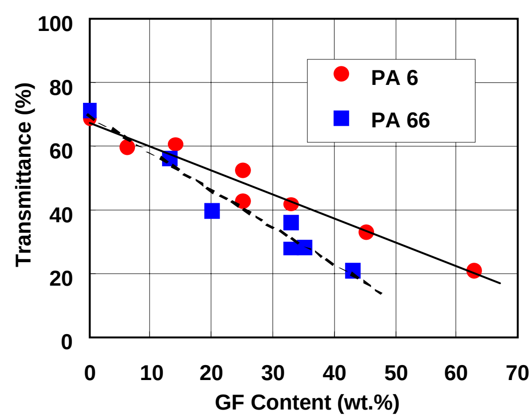

Figure 9. Transmittance of PA 6 vs. PA 66 based plastics with the influence of fiber-glass reinforcement (at wave length 830 nm). Thickness of the specimens is 3.2mm. Color version: natural state

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