BASF Corporation

BASF

OPTIMIZING WELDING TEMPERATURE OF SEMI-CRYSTALLINE THERMOPLASTICS – MEMORY EFFECTS OF NYLON

Abstract

Previously we reported*1 to SPE'99 on the basic principles for optimization of the vibration welding process and presented an analysis of the weld-melt temperature kinetics for linear vibration welding. For this investigation we used the advanced *Thermovision 900®* infrared measurement system*2 for comprehensive, real-time analysis and thermal imaging. Under optimized processing conditions for vibration (linear and orbital) and hot-plate welding technologies, the tensile strength of welded nylon 6 butt joints is equal to or 14% higher than the tensile strength of the base polymer (matrix). For optimized vibration welding conditions, the maximum temperatures of the weld-melt (in inter-phase) were significantly above (85 - 90 °C) the melt point of the welded nylon 6 and nylon 66 (T_m = 223 °C and 261 °C, respectively).

For PP based plastics, J. Vetter and G. W. Ehrenstein observed *3 an increase in the maximum temperature in the weld-melt / in weld inter-phase of not more than 10 °C above the melting point (T_{mp}). In their report to SPE'99, the authors discussed the results of the physical modeling for semi-crystalline HDPE, showing the values of maximum temperatures in the weld inter-phase above 250 °C compared to melting point (T_{mp} = 126 °C). Ch. Bonten presented*4 to SPE'99 his analysis on the mechanisms active in weld interface of semi-crystalline thermoplastics (HDPE and cross-linked polyethylene PE-X). Mechanical performance of welded joints was affected by crystallization across the boundary layer and weld-melt temperature kinetics (above melting point T_{mp}).

For a better understanding of the role and influence of the temperature of the melt (in injection molding) and weld-melt (in welding) on mechanical performance of semi-crystalline molded (welded) thermoplastics, we performed a comparative study for nylon 6 and nylon 66 (non-filled and fiber-glass reinforced) plastics. Mechanical performance of injection molded and welded nylon was evaluated using static (tensile, burst) and dynamic (impact, DMA) tests. The static tensile and dynamic mechanical (DMA) properties were evaluated at a wide range of end-use temperatures, typical for welded nylon parts in automotive under-the-hood, small engines for lawn & power, and similar applications. Melt temperatures (for an injection molding) were varied from 225 °C to 310 °C. These values are significantly above (up to 87 ^{0}C) the melt point of nylon 6 (T_{mp} = 223 °C).

Presented results will help product developers, designers, technologists, and manufacturers, by giving them suggestions on the optimized temperature conditions for the melt and weld-melt inter-phase area.

Introduction

Short fiber-glass reinforced nylon based plastics are the materials of choice for a variety of welded structural components in automotive under-the-hood, lawn and garden and power tool applications. For optimized design of welded hollow components, we need to apply a wide variety of engineering properties for reinforced thermoplastics and welded joints too. Comprehensive studies of the mechanical performance of welded polyamide 66 with respect to plastic composition were published by H. Potente, M. Uebbing and E. Lewandowski [4]. A comparative study of nylon 6 and nylon 66 welded joints, influenced by temperature and moisture, was published by I. D. Froment [5]. These studies [4-5] presented results on mechanical performance of nylon 6 and nylon 66 joints which were applied [6-8, etc.] in the design of vibration welded air intake manifolds, resonators, etc. Reported in [4-8] are tensile strength data for welded joints; the data are very similar for both plastics (nylon 6 and nylon 66) and are equal to 65 - 72 MPa (for 30-35 wt.% fiberglass reinforcement).

In our reports to ASM'95 [9] and SPE'96 [10], we analyzed the mechanical performance of nylon 6 and nylon 66 joints with respect to various welding parameters, such as amplitude, clamp pressure, melt

---

*1 – reference [1];
*2 – *Thermovision 900®* is the trade name of FSI / AGEMA (Inframetric);
*3 – reference [2];
*4 – reference [3].

down, thickness of inter-phase and cooling and hold time. Under optimized welding conditions, the tensile strength of welded nylon butt joints was equal to or 14% higher than tensile strength of the base polymer (matrix). The same mechanical performance of the welded nylon was seen for orbital vibration welding technology also [1]. D. Grewell, in a comprehensive study for the orbital welding technology [12], repeatedly achieved a similar [1, 9-10] tensile strength for nylon 6 joints [*1].

The observed increase [1, 9-10] in the tensile strength of welded butt joints (from 72 up to 85,6 MPa for 33 wt.% fiber-glass reinforcement) was explained by the following:

- local reinforcement in the weld inter-phase, as some fibers (oriented randomly) are crossing the weld interface (Figure 1);
- optimized thermo-mechanical and weld inter-phase formation (melt-down, thickness of inter-phase) for re-melted layers of plastic(s) being joined;
- diffusion of the joined layers.

Remarks on Processing Temperatures -- Melt (Molding) and Weld-Melt (Welding)

At the initial phase of our investigation [9-10], due to technical limitations, we were not able to evaluate the time-temperature kinetics at the weld inter-phase (T_m). Later we developed time-temperature kinetics data for the weld-melt inter-phase during the linear vibration welding process for various nylon 6 and nylon 66 joints. Parts of this data have been published [1, 13]. The temperatures of the weld-melt T_{mw} (in weld inter-phase for 33 wt.% fiber-glass reinforcement) at the steady state were significantly above (of 85-90 °C) the melting points (T_{mp}) of nylon 6 and nylon 66 (Table 1). The melting point value (for the same plastic) can vary as much as 10 °C depending on the method of measurement (Tables 2-3). Observed weld-melt temperature (T_{mw}) increase [1] is in sufficient correlation with the data presented in [3] and is in some disagreement with the part of data published in [2].

The manufacturers recommended molding (melt temperature T_{mi}) conditions for various fiberglass reinforced nylon 6 plastics are very similar (Table 3, [14and Trade Literature]). All melt temperatures T_{m1} and T_{m2} , recommended (by "manufacturer 1" and "manufacturer 2" respectively) are higher than melt point temperature for non-reinforced nylon (T_{mp}). Some small differences between T_{m1} and T_{m2} values were disclosed for two grades only: for the non-reinforced and highly fiberglass reinforced (50 wt.%). Temperature difference Δ_m =(T_{mi} - T_{mp}) increases monotonically (from 17-47 to 58-82°C) with increasing short fiberglass content from 0 to 50 wt.% (Table 3).

Similar values of the weld-melt temperature (T_{mw}) may also be obtained using recommendations developed for hot plate technology [1, 15]. For optimized hot plate welding of semi-crystalline plastics, H. Potente and A. Brubel recommended keeping the hot plate / tool temperature T_{ht} above (of 70 °C) the melt point T_{mp} of the welded plastic [15]. For optimized hot plate welding conditions it is necessary to keep the hot plate / tool temperature T_{ht} slightly higher ($T_{ht} > T_{mw}$, by 10 °C approximately) than the weld-melt temperature (T_{mw}) of the welded plastic, due to heat losses between "heating" and contact phases of the hot plate processing process [1, 13].

Data is shown in Tables 1-3 for the values of processing (molding and welding) temperatures (T_{mw}) showing that optimized mechanical performance of nylon based plastics was achieved at a sufficient higher melt temperatures ($T_{mw} >> T_{mp}$). For semi-crystalline plastics, these effects may be related to the physicochemical characteristic of the base polymer, one must eliminate the influence of impurities, additives, short fiber-glass reinforcements, nucleating agents, and crystalline memory [13, 16]. Some effects of increasing values of T_{mp} for linear welding conditions may be related to influence of the clamp pressure (p_w) at weld-melt (inter-phase) area.

From a thermodynamic point view, the melting point (T_{mp}) is the temperature at which the crystal and the melt are in equilibrium. For theoretical considerations, the last vestige of crystallinity disappears at that temperature. The melting point temperature (T_{mp}) for nylon, reported by a several laboratories and using a number of techniques, has been summarized in [14]. For nylon 6 the melt point temperature (T_{mp}) values may range from 215 to 230 °C [14, 17. and Trade Literature]. We used the melting point (T_{mp}) value equal to 223 °C for nylon 6 and 261 °C for nylon 66 (Table 1). The freezing points are frequently about 30°C lower than the melting points (T_{mp}). The following solidification temperatures can be used for nylon [14]:

- nylon 6, from 170 to 190 °C;
- nylon 66, from 215 to 240 °C.

In some laboratory experiments for nylon 6, crystallization has been carried out much closer to the melting point (T_{mp}) at 205 °C to 215°C [16].

We did not find published correlation between plastics composition (level of fiber-glass reinforcement, fillers, impact modifiers, etc.), the weld-melt temperature T_{mw} (or for hot tool temperature T_{ht}), weld clamp pressure (p_w) and welding time (t_w) for linear vibration and hot-

[*1] - Capron® 8233G HS from AlliedSignal, Inc. injection molded in the plaques 102 mm x 71 mm x 6.25 mm.

melt [17] (extrusion or in-mold injection) welding technology.

Experimental

Materials

The thermoplastics analyzed in this investigation (injection molding, welding and testing) were heat stabilized nylon 6 and nylon 66. Limited data will also be presented for nylon 46. Commercially available nylon 6, nylon 66 and nylon 46 plastics are widely used for design of the welded structural components. These plastics have a wide loading range of fiberglass (GF) reinforcement, mineral fillers (MF), etc. (Table 4).

Because the fiberglass reinforcements and mineral fillers possess different thermal properties (thermal conductivity, heat capacity, etc.) from the base polymer, they affect the thermal properties of the plastic's heating, welding and cooling time. Melting point data may vary because the method of measurement, oligomer contents, additives, reinforcements, fillers, and crystalline form can alter the result (Tables 1-3) [14].

Test Procedures

For quality control and quality assurance of the welded components, tensile, impact and burst tests are usually applied [1-12, 15]. One very important parameter needed for the design of weld-bead(s) is the tensile strength of a welded joint at break (with the influence of processing technology including time-temperature effects).

The tensile strength of a weld at 23 °C ("dry as molded" and "welded as dry" conditions) is "key data"- the first step in the plastic component design, welding process optimization, and comparative analysis of material suitability for welding application. Not all thermoplastics, static (tensile) and dynamic (Izod, Charpy) properties are sensitive to the fine structural changes of thermoplastics related to processing (molding and welding) temperatures.

For welded butt joints, basic tensile test data was obtained from rectangular specimens (10 mm by width, 125 mm by length) cut and machined from welded plaques (Figures 3-4) and multi-purpose universal welding & testing specimens (Figure 5). For each welding processing condition, a minimum of five specimens were tested using ISO 527 (or ASTM D 638) procedures. All tensile and burst test results were used for performance optimization. Samples with high tensile strength were selected to perform the morphology analysis in the weld zone (inter-phase). ISO 537 (or ASTM D 732) test procedures were used for evaluation of the shear strength of welded lap joints (Figure 6).

Because the fiberglass reinforcements and mineral fillers possess different thermal properties (thermal conductivity, heat capacity, etc.) from the base polymer, they affect the thermal properties of the plastics and the heating, welding and cooling times. Melting points data may vary because the methods of measurement, oligomer contents, additives, reinforcements, fillers, and crystalline form can alter the result [14].

Differential scanning calorimetery (DSC) methods were successfully applied to an analysis of the structural changes in nylon [19]. In addition to traditional evaluation methods [1-12, 15-16] dynamical mechanical analysis (DMA) was also applied in this investigation. A Rheometrics RDA-II torsional rheometer was used with the torsion rectangular geometry. All conditions were in accordance with ASTM D 5279. Sample size was a bar nominally 60 mm long, 10 mm wide, and 4 mm thick. A frequency of 1 Hz and strain of 0.05% were used. Temperature steps of 5 °C were made from – 50 °C to 210 °C with an isothermal time at each temperature step of 3 minutes.

Burst tests (static, cyclic and dynamic) are typical for the final phase of the performance evaluation of the welded components. The burst test data (ultimate pressure, failure analysis) are used in optimized performance evaluation of the welded hollow / multi-shelves components, when requirements to part sealing and hermetic are critical. Burst test data permit evaluation of material behavior, optimization of molding and welding procedures (including time-temperature profile), improved accuracy of the FEA of the welds and joined parts, better sealing / hermetic, etc. under end-use loading conditions. Dynamic burst test is more sensitive to structural changes of the polymer, and possible defects, than is static tensile test due to non-linear stress-strain distribution in the weld areas, and strain rate effects.

Advanced Models of the Welded Joints for Thermo-Mechanical Analysis in Plane / Linear and Curvilinear Welding Areas

Correct design of plastic part and welding processes require proper design of various weld beads (Figure 2), specimens, models and properly simulated welding processing conditions (including temperatures in inter-phase). The test and processing conditions should also be similar to manufacturing and end-use conditions.

Utilized in this investigation are molded and welded specimens / systems, applied test and measurements methods, design principles of the joints, that are in a process of continuous improvement. Presented below (Figures 4-8) are welded joints (butt and lap / shear) models, designed with the influence of the specifics related to the real time-temperature analysis and image handling, and welding processes simulation for critically loaded plastic components, such as welded air intake manifolds (Figure 3).

Optimizing Plane Models of the Butt Joints: from Plaques to Multi-Purpose Systems

In the basic study on welding process optimization and mechanical performance evaluation, we used the recommendations for the air intake manifolds butt joint design, consisting of two beads 4 mm and 6 mm thick and welded together (Figure 4). Sizes (length × width x thickness) of the injection molded rectangle plagues are as follow:

- 150 (or 100) mm × 60 mm × 6.25 mm;
- 150 (or 100) mm × 60 mm × 4 mm.

Sizes (length × width) of the welded plagues are 150 (or 100) mm × 120 mm (approximately). Weld area is equal to 600 (or 400) mm^2 respectively for the plaques 150-mm and 100 mm long.

For specific design applications (highly stressed welded components) we need to evaluate the influence of weld-bead design (height of a bead), fiberglass and fillers orientation, and injection molding conditions on tensile strength of the butt joints. It is possible to utilize in these applications the T-type /shape butt joints by welding together above-mentioned injection molded rectangle plaque (thickness = 4 mm) and T–shape component with the bead 6 mm thick (Figure 5). The thickness of the plaques (weld beads) may be varied (the following thickness is also available: 1,6 mm and 3,2 mm). Maximum cross-section in the weld areas for these specimens is equal to 600 mm^2 (for weld beads 4 mm and 6 mm thick).

Evaluation of the butt joint performance by using the rectangular plaques (Figure 4) and T-shape elements (Figure 5) has a lot of the advantages: simple molding and welding tools; availability of the injection molded plaques, etc.; convenient configuration and sizes of the test specimens. These specimens may be successfully welded in a small (Mini-Welder[*1] type) and midsize welding machines only (due to limitations on the minimum clamp force). For larger welding machines these specimens are too small (and clamp pressure is very high), because minimum clamp force is more than 3 kN.

A special "multi-purpose universal weld & test system" has been designed for more accurate modeling of the welding process and evaluation of joints performance (Figure 6). This system consists of two, multi-purpose, octagonal specimens that are welded together. The following basic concerns and problems, design and technology issues have been taken into account for design of this universal welding & testing system:

- possibility to model welding conditions similar to those recommended for use in the production;
- correlation of sizes and design of plastic parts and welded specimens with the size of available welding machine, value of minimum clamp force, etc;
- possibility to have similar plastic state in weld bead areas (polymer structure and morphology, mechanical properties, etc.) for injection molded plastic parts and welded specimen;
- multi-purpose application of developed weldability data for plastic part design and optimized welding processing conditions.

Octagonal configuration and design advantages of universal specimen (Figure 6) allows evaluation of efficiency of injection molding and welding process for the butt joint with the various thickness of the beads (by combining the following thickness: 2,5 mm; 4,0 mm; 5,0 mm and 6 mm). Weld area is equal to 3,600 mm^2 (approximately). "Universal weld & test system" may be utilized in industrial applications for design, material and process optimization, where mid- and full-size welding machines are used. The shape of the specimen (octagonal) and the thickness of the beads may vary. These multi-purpose universal specimens may be used for orbital vibration, hot plate, infrared (diffusion) welding also. The mode of the straight butt joints (Figure 4) and the universal welding & testing system (Figure 6) are convenient for direct weld-melt temperature measurement and image handling, using infrared systems.

Universal Model of the Lap / Shear Joints

More complicated is the test and weld strength evaluation of the lap / shear joints (due to non-uniformed clamping conditions, presence of additional flexural effects for welded together two plane plaques, and fiber-glass orientation - "skin effects"). Special injection molded (teeth shape) plaques may be used for the shear / lap joints design (Figure 7). Basic shear joint consists of the two beads 4-mm and 6 mm thick (the following thickness of the weld bead is also available: 1,6 mm; 2,5 mm; 3,2 mm and 5,0 mm).

A New Model for Welding Process and Material Analysis in Curve-Linear Joining Areas

The curve-linear model of the butt joints (Figure 8) was designed to analyze thermo-mechanical material

[*1] – Mini-Welder is trade name of the welding machine from the Branson Ultrasonics Corporation.

behavior at welding processing conditions that are similar to conditions used in design and manufacturing of air intake manifolds. Welded manifolds typically consist of 2-4 injection molded pieces / parts that are welded together (Figure 3). Shape of the welds at a runner area is curve-linear. Design of the curve-linear parts requires additional information on clamp pressure, meltdown, tolerances, gaps, and temperature distribution at curve-linear areas.

At the current time, reported [1-13, 14] weldability data of semi-crystalline plastics was developed for the plane welded joints. We did not find similar weldability data for welded nylons (or other thermoplastics) at curve-linear joining areas.

It is possible to simulate curve-linear design and processing conditions by welding together disc and plaque with half-hole (Figure 8). For this mode we used an injection molded disc (thickness = 4 mm, diameter d_{disc} = 100 mm) and a special plaque (thickness = 6.25 mm). Sizes (length x width) are 150 mm x 100 mm and nominal diameter of the half-hole in the plaques d_{hole} = 100 mm. Diameter d_{hole} was varied (from 100 mm to 101 mm). The simulation of various tolerances and meltdown permit us to optimize mechanical performance of the weld in curve-linear joining areas. Sizes of joining curve-linear elements (disc and plaque) can be varied.

The following advantages and limitations are for the discussed models (Figures 4-7):

- All three models of the butt and lap / shear joints permit analysis of vibration welding process and material behavior at various motions (longitudinal, perpendicular to part thickness and by an angle).
- For curve-linear joint areas is it possible to apply vibration motions perpendicular to thickness of the curve-linear wall only (Figure 8).

Temperature Kinetics at the Weld-Melt (Weld Inter-Phase) -- Real Time-Temperature Analysis and Image Handling

Weld-melt (melt-pool) temperature (T_{mw}) is one of the most important parameters affecting the performance of any welded joints (butt , lap / shear or mixed mode) during the joining process. For the weld-melt temperature (T_{mw}) measurement during the welding process we used *Thermovision 900®* infra-red (IR) system for comprehensive, real time analysis and image handling (Figures 9-10). We measured the time-dependent temperature (t_w - T_{mw}) distribution and melt-weld (mw) propagation in the weld interface (at five local areas with the same size) during the linear vibration welding process (Figure 9). The results were obtained at various longitudinal linear vibration welding conditions (amplitude-pressure-melt-down, heating and cooling / hold time), at vibration welding frequency =210 Hz.

Figure 10 shows time-temperature profiles (t_w - T_{mw}) for the various grades / compositions of nylon 66:

- non-reinforced / non-filled (Figure 10 a);
- short fiber-glass reinforced (Figure 10 b);
- short fiberglass reinforced and mineral filled (Figure 10 c).

Time-temperature kinetics for non-reinforced / non-filled plastic is described by a smooth (t_w - T_{mw}) curve (Figure 10 a) for both nylon (6 and 66). Duration of pre-heating phase, when temperature of the melt-pool (T_{mw}) will reach level above melting point (T_{mp}) is equal to 6 and 8 sec for nylon 6 and nylon 66 (respectively). Heating generation process (t_w - T_{mw}) for short fiberglass reinforced plastics is more dynamic (Figure 10 b). The 2-3 second plastic pre-heating phase is too short for the heat to penetrate through all inter-phase areas; an additional 4-6 seconds are needed for this purpose. Reinforcement and fillers affect the thermal properties of nylon. Specific heat increases for short fiber-glass reinforced plastic (from 1,5 to 1,7 J/gK with increasing fiber-glass content from 0 to 30 wt.%), thermal conductivity decreases (from 0,24 to 0,23 for nylon 6 and from 0,27 to 0,21 for nylon 66 at the same range of fiber-glass reinforcement) [14].

The distribution of weld-melt temperature (T_{mw}) in local areas was not isochronal (uniform in duration); it was dependent on the flatness of welded surfaces, nest / welding tool design and heat transfer-out. When the linear vibration welding machine is shut off, the weld penetration continues to increase because the clamp pressure causes the molten interface to flow until it solidifies. During the shutting off phase the interface, temperature has a tendency to increase (by an average of 30-40°C, see Figure 10 a. b).

The maximum temperature ($T_{mw,\ max}$) of the weld-melt (melt-pool) was equal to the melting point of welded polymers or blends + (85-100 °C). The results in this study are close to data presented in [3] and slightly different from the hot tool temperature (T_{th}) data for the hot plate technology [15]. These differences may reflect the difference in methods used, calibration, measurement procedures, and effects observed and analyzed during this investigation.

Memory Effects in Nylon

Melt-Memory Effects

A factor affecting the crystallization process in slow, or moderately slow, crystallizing polymers is called the "crystalline memory" and its results are usually lumped together under the umbrella of "memory effects".

It is manifested as the formation of a defined degree of macromolecular order in the welded interface / phase, as well as a rise of the melting temperature (T_{mp}) of the semi-crystalline systems in the melt-pool [16, 18]. Melting under conditions that do not completely erase the “crystalline memory” may result in microscopic or submicroscopic fragments of previous crystals remaining in the melt, and during cooling of the melt serve as the predetermined nuclei for fresh crystallization. The number and size of the nuclei which remain in the melt depends on the following three factors [17]:

- the temperature of any previous crystallization (since the higher this temperature the more perfect the crystallites and the higher their melting point T_{mpi});
- the temperature of melting (the higher this temperature the more complete id destruction of the crystallites formed previously;
- the duration of time (t_{mi}) the specimen of semi-crystalline plastic is held in the molten sate (since the dispersal of the crystallites is not an instantaneous process).

For welding of thermoplastics “memory effects” reflect the thermal history of the molded part and, in addition, are affected by the melt temperature (T_{mp}) and welding time (t_{wm}) spent in the molten state. The highest temperature at which the polymer crystal may survive is the equilibrium melting point T_{mo} . For nylon 6, the equilibrium melting point (T_{mo}) may occur at about 270 °C. Other the equilibrium melting point (T_{mo}) values obtained for nylon 6 by various extrapolations range from as low as 215 °C to as high as 306 °C.

Anneal temperature T_a (the temperature at which the melt is kept in order to remove the nuclei) must be higher than T_{mo} . Anneal temperatures (for nylon 6) as low as 260 °C were sufficient to eliminate memory effects, but 270 °C and even 280 °C are now recommended as temperatures at which memory effects are completely erased. In all these, it is assumed that $T_a \geq T_{mo}$. Similar results [16] were observed (in pellets) of several nylon (Tables 5-7).

Melt-Temperature – Weld-Clamp / Mold Pressure Relationship

During frictional (linear and orbital) vibration and hot plate / tool welding processes, mating parts are clamped under the applied pressure (p_w), which is a very important parameter for the mechanical performance of the weld. The vibration welding process, depending on the part size, tolerances and mechanical properties of welded nylon, will typically operate with clamp pressure (p_w) of approximately 3.5 MPa [5-6, 8, and 14]. Variations in the applied pressure (p_w) of the amorphous phase of semi-crystalline polymers, may affect the glass transition (T_g), melt (T_{mp}) and annealing (T_a) temperatures. It is difficult to measure the glass transition temperature (T_g) exactly. Melting point temperatures (T_{mp}) are 150 °C above the glass transition temperatures (T_g). The glass-transition temperature (T_g) depends upon the measurement technique and may vary from 41 to 75 °C [14, 16].

Pressure-volume-temperature (PVT) data for nylon 6 and nylon 66 plastics was primarily developed in a range of pressures from 50 to 200 MPa (Table 8). The glass-transition temperature (T_g) increases by 80-85% with increasing pressure from atmospheric to 200 MPa. For nylon 66 the effect of pressure (p) on melting point (T_{mp}) and crystallization temperature (T_{cc}) is summarized in [14], where T_{mp} and T_{cc} in (°C) and p in MPa[*1]:

$$T_{mp} (f_p) = 266{,}8 + 0{,}2285\, p \qquad (1)$$

$$T_{cc} (f_p) = 243{,}1 + 0{,}1871\, p \qquad (2)$$

We did not find similar data (equations) for nylon 6.

The molding pressure ($p_{m.}$) profile may vary as a function of melt temperature (T_m), mold-tool geometry and plastic composition. Injection and packing pressures are generally within the range of 3,5 to 12,5 MPa. For optimal welding conditions (linear vibration or orbital vibration welding) a nominal clamp pressure ($p_{w,\ nom}$) in weld inter-phase is within the range of 1,2 to 2,2 MPa (approximately). The influence of clamp or molding pressure on the melting point (T_{mp}) will be not significant (in a range of accuracy of temperature measurement technique / method).

Melt Temperature: Relationship to Crystal Structure and Mechanical Performance

The high melt-pool, and mold (cavity) temperatures delay freezing to facilitate filling long, thin sections. (this is similar to localized re-melting and melt-pool formation processes in weld bead areas). It is also encourages greater crystallization of the semi-crystalline resins, which affects both mechanical properties and dimensions. Relations between processing (molding - T_m, and welding- T_{mw}) temperatures for non-reinforced / non-filled nylon 6 are presented in Table 9.

Optimized mechanical performance of welded butt joints (Table 10) was achieved at maximum for a weld-melt (melt-pool) temperature above (from 47 °C to 70 °C) of the crystalline melting point (Table 9). Observed values of the maximum temperatures of the weld interface / melt-pool (T_{mw} , Figures a, b, c) are very close to the anneal temperature (T_a) for evaluated nylon 6 specimens (Tables 5-7, 9). These results help explain

[*1] – Usually 1,0 MPa = 10 bar ~ 145 psi

observed "memory effects" for welded butt joints and for injection molded nylon plastics.

The possibility that "memory effects in the weld inter-phase" can dominate is born out by the results of the influence of injection molding processing conditions for nylon 6 plastics. We evaluated the influence of injection molding conditions (at various melt temperature from 225 to 310 °C) on mechanical and thermal properties of two grades of nylon 6 plastics (non-reinforced / non-filled and 33 wt.% fiber-glass reinforced). Reported data on mechanical performance include stress at yield and break and the corresponding strains and notched Izod data (Tables 11-12) at room temperature conditions (23 °C).

The decrease of tensile strength at yield as a function of mold temperature (T_m) is shown in Table 11. Strains at yield, strength at break and notched Izod data are not sensitive to molding conditions. Strain at break reaches maximum value (equal 65%) at 270 °C; at low molding temperatures (225-235°C) non-reinforced nylon 6 is very brittle (strains at break are equal to 27-32%, see Table 11). The increase of maximum strength, notched Izod and elastic modulus data for fiberglass reinforced (33 wt.%) plastic is shown in Table 11. Strain at break reaches maximum value (equal 3,53%) at 270 °C; at low molding temperatures (225-235 °C) fiber-glass reinforced (33 wt.%) nylon 6 is very brittle (Table 12).

Injection molded nylons have lower orientation and are predominantly spherulitic. Nylon 66 crystallizes much faster that nylon 6. At temperatures close to the melting point temperature (T_{mp}), the crystallization rate is low, and large crystal sizes can be obtained. At lower temperatures far below T_{mp} , the crystallization rate is faster, but smaller crystals are formed. The presence of "memory effects" aggravates the problem of separating crystallization effects in nylons, as faster nucleation due to presence of self-nuclei (residual nuclei) as a factor in initial crystallization. Injection molding processes generally involve non-isothermal heating, and cooling rate and shearing conditions also affect crystallization. Orientation is usually restricted to a surface layer because of the high shear rates near the surface during processing. An improved understanding of physical and mechanical properties and their relationship to processing variables requires a knowledge of crystal structure and morphology of nylon based plastics.

Mechanical performance data correlate well with physical structures of evaluated nylon 6. Nylons can occur in more than one crystalline form (α and γ), depending on the conformation and packing of the polymer chains during polymer crystallization. Transformation between the phases occurs upon processing, annealing, and mechanical stresses. Profile analysis of the X-ray diffraction peaks corresponding to the α and γ crystalline forms in semi-crystalline nylons permits determination of the crystalline fractions.

For molded nylon 6 three different crystal structures were observed based on a different dependence of their properties on density. The α form crystals were obtained from crystallization at higher temperatures or annealing; γ crystals were obtained at lower temperatures. Quenching gave a disordered, pseudo-hexagonal form, which is called γ^* form [16-17].

Injection molding forces molten nylon at high pressure into temperature controlled molds. This results in a three-layered sandwich-type structure, a very thin nearly amorphous skin (with a thickness from 0,1 mm to 1,0 mm), a relatively high crystallinity core and less crystalline inter-phase layer. The different level of crystallinity and molecular orientation leads to very complex stress-strain distribution through all these three layers. Typically meltdown value for vibration welded manifolds is at range 1,5-1,8 mm. Part of a thin skin will be removed to melt-flash at initiated phase of heat propagation in weld areas. The melt-pool formation will involve the inter-phase & core areas also.

The crystalline index (CI) slightly decreases with increasing molding temperatures from 225 °C to 310 °C (Figure 11). The width of the crystalline peak in X-ray diffraction is related to the size of crystals (as measured by the index of crystalline perfection (ICP). For nylon 6 the ICP reaches a local minimum (Figure 12) at the maximum strain at break (eliminating the previous brittleness). Because ICP is free of the possible errors due to sampling and measurement procedures (sample mounting and instrumental angular correction), it can be measured rather precisely and is used in conjunction with CI (crystalline index) and CSP (crystallite size and perfection).

Table 13 provides data on glass-transition temperature (T_g) for nylon 6 with the effects of molding (melt) temperatures. In the present report all T_g values (Table 13) have been taken from DMA curves. Furthermore, the glass transition temperature T_g is far more sensitive to the frequencies used in its determination than T_{mp} and, at any frequency or heating rate the temperature interval is far wider than that of the melt point temperature (T_{mp}). The glass transition temperature (T_g) decreases slightly (from 43,1 to 38,7 °C) for non-reinforced nylon 6. These results are in a good correlation with data for T_{cc} (temperature of crystallization upon cooling from the melt) as function of melt anneal temperatures (T_a) [16]. For fiberglass reinforced (33-wt.%) plastic T_g reaches local maximum at 260 °C and all temperature changes were not significant. Kinetics of the dynamic mechanical behavior of nylon as function of molding (melt) temperatures is shown in

Tables 14-15. The dynamical shear modulus shows different behavior for evaluated plastics under the influence of molding and test temperatures:

- for non-reinforced plastic value of ***G'*** decreases at all test conditions;
- for fiberglass reinforced (33 wt.%) ***G'*** reaches a local maximum at melt temperature 280 °C approximately) for all test conditions (- 40; 23 and 120 °C).

The changes of the ***G'*** modulus are 4-5% for fiberglass reinforced plastic and 9-10% for non-reinforced plastic (DMA is the key test method, which provides kinetics of deformation properties).

Melt Temperature: Relation to Mechanical Performance of Hot-Melt / Extrusion Welding

Hot-melt, part and mold temperatures are critical factors affecting mechanical performance when joining nylon parts. A multi-cavity injection molding process also requires optimized hot-melt temperature at the joining/sealing phase [19-20]. The sealing phase (Figure 13) is a key element of this technology. For the injection-molded parts, 33 wt.% nylon 6 was used, and un-reinforced, un-filled nylon 6 was used for the hot-melt. For the sealing phase, we used optimized (see "memory effects") molding hot-melt temperatures (Tables 5-7, 9). At optimal temperatures (for hot-melt, and joined parts 1-2) an inter-phase is formed (14). This multi-layer structure in the joint provides high levels of mechanical performance, when equal strength principles were realized in the design of the joined parts.

Concluding Remarks

- Optimal mechanical performance of nylon joints was achieved using weld-melt temperatures above the melting point(s) of various nylon-based plastics.
- Studies on heat generation and melt propagation in the inter-phase area demonstrate the dynamics of temperature distribution in the inter-phase area and overall. Time-temperature kinetics depends on the plastic composition, because reinforcements and fillers affect the thermal properties of nylon.
- The distribution of weld-melt temperatures in localized areas is not isochronus; it is dependent on the flatness of the welded surfaces, welding tool design and heat transfer.
- The maximum temperature of the weld-melt (melt-pool) is 85-100 C above the melting point of welded polymer(s).
- Melt-point temperature elevates slightly due to applied clamp pressure, and decreases slightly for plastics molded at high temperatures.
- Increase of melt-weld temperature over the melt point for plastic correlated well with recommended molding temperatures for nylon 6 plastics. Manufacturer recommendations on molding temperatures may be applied for optimized welding conditions of various nylon plastics.
- The relations between optimized welding / molding temperatures and "memory effects" will allow technologists to optimize processing conditions.
- The measured glass transition temperature varies with the technique of measurement.

Acknowledgments

The author wishes to thank Nanying Jia and Eric Day for testing, Boris Chernyavsky for modeling and C. Roth for help in preparing this study for publishing. Special thanks go to Shaul Aharoni and Sanjeeva Murthy for knowledge and discussion on the "memory effects".

References

1. Kagan, Val A., *"Joining of Nylon Based Plastic Components – Vibration and Hot Plate Welding Technologies"*, SPE/Antec'99 Conference Proceedings, Vol. 1, pp. 1349-1359, (1999).
2. Vetter, Jorg, Ehrenstein, Gottfried W., *"Biaxial Vibration Welding of Polypropylene*", SPE/Antec'99 Conference Proceedings, Vol. 1, pp. 1344-1348, (1999).
3. Bonten, Ch., *"A New Hypothesis to Describe the Acting Mechanizm in a welded Joint of Semi-Crystalline Thermoplastics*", SPE/Antec'99 Conference Proceedings, Vol. 1, pp. 1376-1380, (1999).
4. Potente, H., Uebbing, M. and Lewandowski, E., *"The Vibration Welding of Polyamide 66",* Journal of Thermoplstic Composite Materials, Vol. 6, pp. 2-17, January, (1993).
5. Froment, Ian D., *"Vibration Welding Nylon 6 and Nylon 66 – A Comparative Study*", SPE/Antec'95 Conference Proceedings, Vol. 1, pp. 1285-1289, (1995).
6. Nelson, W. Kenneth, *"Vibration Welding: A Low Cost Assembly Process for Thermoplastic Intake Manifolds*", SAE International, SP-950230, 10 p., (1995).
7. Lee, Jordan, Roessier, Lisa, *"Vibration Welded Composite Intake Manifolds – Design Consideration and Material Selection Criteria",* New Plastics Applications for the Automotive Industry, SAE International, SP-1253, pp. 27-43, (1997).
8. Matsco, M. M.,*"Multishell Technology for Plastic Part Manufacturing",* Proceedings of Structural Plastics'95, SPI Technical Conference and New Product Design Competition, pp. 128-134, (1995).
9. Kagan, V.,Lui, S.-Ch., Smith, G., *"The Effects of Fillers and Reinforcement on Vibration Welding of*

Nylon 6", Proceedings of ASM's Material Congress, Cleveland, (1995).
10. Kagan, V., Lui, Siu-Ching, etc., *"The Optimized Performance of Linear Vibration Welded Nylon 6 and Nylon 66 Butt Joints"*, SPE/Antec'96 Conference Proceedings, Vol. 1, pp. 1266-1274, (1996).
11. Kagan, V., etc., *"Performance of Vibration Welded Thermoplastic Joints*", US Patent # 5,874,146, (1999).
12. Grewell, David, *"An Application Comparison of Orbital and Linear Vibration Welding of Thermoplastics*", SPE/Antec'99 Conference Proceedings, Vol. 1, pp. 1365-1369, (1999.
13. Kagan, Val A., *"Advantages of Welded Nylon for Powertrain Application: Linear Vibration, Orbital and Hot-Plate Joining Technologies",* - New Materials & Development Processes, Global Powertrain Congress - GPS'99, (1999).
14. Melvin I. Kohan, *"Nylon Plastics Handbook",* Hanser Publisher, New York, 631 p., (1995).
15. Potente, H., Brubel, A., *"Welding Behavior of Filled and Reinforced Thermoplastics with Hot Plate Welding",* SPE/Antec'98 Conference Proceedings, Vol. 1, pp. 1062-1066, (1998).
16. Aharoni, Shaul, *"Increased Glass Transition Temperature in Motionally Constrained Semi-Crystalline Polymers"*, Polymers for Advanced Technologies, Vol. 9, pp. 169-201, (1998).
17. Aharoni, Shaul, *"n-Nylons: Their Synthesys, Structure and Properties"*, John Willey & Sons, New York, 598 p., (1998).
18. Khanna, Y., Reimschuessel, A.,*"Memory Effects in Polymers",* Part I: Orientational Memory in the Molten State: Its Relationship to Polymer Structure and Influence of Re-Crystallization Rate and Morphology., Journal of Applied Polymer Science, Vol. 35, pp. 2259-2268, (1988).
19. *"Rotating Molds Unlock Potential for Car Manfolds",* Modern Plastics, pp. 29-30, February, (1999).
20. Destefani, J., *"Manifolds Improvements",* Molding Systems, pp. 34-38, August, (1999).

Key Words

Semi-crystalline thermoplastic, nylon, polyamide, welding, joining, linear, orbital, vibration, frictional, hot-plate, butt, shear, joint, test, evaluation, morphology, thermal image, fiber-glass, optimization, temperature profile, glass-transition, melting point.

Phrase Index

Melt-pool – volume of melted plastic(s) between welded parts.

Weld interface – boundary between two fused (mixed) polymers. The thickness of interface is equal to 30 nm (approximately).

Weld inter-phase – re-melted layer(s) of plastic(s) between welded together thermoplastic components. The thickness of inter-phase may vary from 30 to 300 μm.

Weld-melt – molten layer(s) of plastic(s) between together welded thermoplastic components.

Table 1: Maximum Weld-Melt Temperatures ($T_{mw,\ max}$), °C in Weld Inter-Phase for Nylon (33% GF Reinforced by Weight) Based Plastics at Optimized Linear Vibration Welding Conditions [1]

Type of Nylon	Melting Point (T_{mp}), °C	Maximum Melt-Weld Temperature ($T_{mw,max}$) in Weld-Phase / Plane, °C
Nylon 6	223	270 ~ 285
Nylon 66	261	295 ~ 320

Table 2: Manufacturers Recommended Molding / Melt Temperatures for Nylon 6 Based Plastics [14]

Type of Plastics	Melt Temper. (T_m), °C	Melt Point Temper. (T_{mp}), °C	Temper. Differences $\Delta_m = T_m - T_{mp}$
Homopolymer	240 ~ 270	215	25 ~ 55
Impact Modified	250 ~ 280	205 ~ 215	45 ~ 65
Fiber-Glass Reinforced	255 ~ 305	215	40 ~ 90
Mineral Filled	270 ~ 305	215	55 ~ 90

Table 3: Manufacturers Recommended Molding / Melt Temperatures For FiberGlass Reinforced Nylon 6 Plastics. Legend: *[1] And *[2] – Recommendations Provided By Manufacturers (1) And (2), Respectively

GF wt.% (by weight)	Melt Temper.*[1] (T_{m2}), °C	Melt Temper.*[2] (T_{m2}), °C	Temperature Differences $\Delta_m = T_{m1} - T_{mp}$
0	240 ~ 270	250 ~ 270	17 ~ 47
14	260 ~ 280	270 ~ 290	37 ~ 57
25	271 ~ 293	270 ~ 290	48 ~ 70
33 (35)	271 ~ 293	270 ~ 290	48 ~ 70
40 (45)	271 ~ 293	270 ~ 290	48 ~ 70
50	271 ~ 305	280 ~ 300	58 ~ 82

Table 4: Composition of Nylon Plastics (% wt., by weight) for a Structural and Welded Components

Type of	Fiber-	Mineral	GF /	Specific

Nylon	Glass (GF)	Fillers (MF)	MF	Gravity g / cm^3
Nylon 6	5-63	12 – 40	15 / 25	1,13-1,15
Nylon 66	5 - 72	15 – 40	16 / 24	1,13-1,15
Nylon 46	15 - 45	10 – 30	16 /24	1,18

Table 5: Memory Effects of Nylon (Virgin Polymer, Non-Reinforced / Non-Filled) Based Plastics (at the Same Heat / Cooling Rate)

Type of Nylon	Nylon 6	Nylon 66	Nylon 46
Melting Point, ($T_{mp,}$), °C	221,6	262	287
Anneal Temperature ($T_{a,}$), °C	270	290	305
Glass Transition Temper., ($T_{g,}$), °C	54,8	63,3	76,7

Table 6: Memory Effects of Nylon (Ground 3 Times, Non-Reinforced / Non-Filled) Based Plastics (at the Same Heat / Cooling Rate)

Type of Nylon	Nylon 6	Nylon 66	Nylon 46
Melting Point, ($T_{mp,}$), °C	218,9	260,1	262
Anneal Temp. ($T_{a,}$), °C	270	290	305
Glass Transition Temp. ($T_{g,}$), °C	51,1	58,7	74,7

Table 7: "Memory Effects" of Nylon 6 Plastics (Non-Reinforced / Non-Filled)

Temperature Conditions	Nylon 6, Virgin Pellets	Nylon 6, Ground 3 Times
Glass-Transition Temperature ($T_{g,}$), °C	54,8	51,1
Melting Point ($T_{mp,}$), °C	221,6	218,9
Anneal Temperature ($T_{a,}$), °C	270	270
Recommended Molding (Melt) Temperature, ($T_{mi,}$), °C	240 ~ 270	240 ~ 270

Table 8: Changes in Glass Transition Temperatures (T_g, °C) as Function of Applied Pressure (p)

Type of Nylon	at Atmospheric Pressure (p_{atm})	at Evaluated Pressure (p_{200}) = 200 MPa,
Nylon 6	52	99
Nylon 66	60	109

Table 9: Relations Between Processing (Molding and Welding) Temperatures Conditions and "Memory Effects" For Nylon 6 Plastics (Non-Reinforced / Non-Filled)

Thermal Properties of Nylon 6 Plastics and Welded Joints (33 wt.% GF)	Temperature in ^{0}C
Melting Point (T_{mp} ,)	223
Anneal Temperature (T_a ,)	270 ~ 306
Recommended Molding (Melt) Temperatures (T_m)	240 ~ 270
Maximum Temperature in Weld Inter-Phase (melt-pool), $T_{mw,max}$	270 ~ 295
Temperature Differences $\Delta_1 = T_m - T_{mp}$	17 ~ 47
Temperature Differences $\Delta_2 = T_{mw,\,max} - T_{mp}$	47 ~ 72
Temperature Differences $\Delta_3 = T_{mw,\,max} - T_a$	0 ~ (- 11)

Table 10: Optimized Mechanical Performance of Nylon 6 Butt Joints at Various Welding Technologies

Fiber-Glass Content (wt. %) for Capron® (Nylon 6 Plastics)	Linear Vibration Welding	Orbital Vibration Welding	Hot Plate / Tool Welding
8202 (0 wt.%)	83,1	83,0	78,2
8231G (14 wt.%)	90,7		-
8232G (25 wt.%)	90,2	90,4	89,8
8233G (33 wt.%)	85,6	87,1	84,5
8234 (45 wt.%)	-		80,3
8235G (50 wt.%)	80,5		-

Table 11: Influence of Injection Molding Conditions (Molding / Melt Temperature) on Mechanical Performance of Nylon 6 (Capron 8202, Non-Reinforced / Non-filled)

Melt Temp. (T_m), ^{0}C	Strength at Yield, MPa	Strength at Break, MPa	Strains Yield, %	Strains at Break, %	Notch Izod J/m
225	84,8	49,9	4,12	27	187
235	82,4	53,5	4,34	32	181
245	80,4	49,2	4,33	54	180
260	79,9	49,3	4,33	55	191
270	80,8	49,5	4,34	65	189
290	80,9	49,2	4,39	48	186
310	80,2	48,5	4,4	48	182

Table 12: Influence of Molding Conditions (Melt Temperature) on Mechanical Performance of Capron 8233G (Nylon 6, GF = 33 wt.%)

Melt Temp. T_m, ^{0}C	Maximum Strength, MPa	Strains at Break, %	Notched Izod, J/m
225	167,1	3,07	617
235	180,2	3,26	674
245	180,9	3,38	692
260	184,1	3,49	759
270	186,4	3,53	764
290	188,1	3,42	766
310	188,4	3,17	710

Table 13: Influence of Molding Conditions (Melt Temperature) on Glass-Transition Temperatures (^{0}C) for Capron 8202 (Nylon 6, Non-Reinforced / Non-Filled)

Melt Temp. (T_m), ^{0}C	Non-Reinforced 0 wt.%	Fiber-Glass Reinforced 33 wt.%
225	43,1	37,7
235	43	38,9
245		38,2
260	42,0	39,2
270	40,7	36,7
290	39,2	37,7
310	38,7	36,4

Table 14: Influence of Molding Conditions (Melt Temperature) on Shear Modulus (***G’,*** MPa) for Capron 8202 (Nylon 6, Non-Reinforced / Non-Filled Plastic) at Various Test Temperatures

Melt Temp. (T_m), ^{0}C	Tested at - 40 ^{0}C	Tested at 23 ^{0}C	Tested at 120 ^{0}C
225	1,010	980	143
235	962	927	128
260	953	915	125
270	930	889	117
290	948	905	120
310	938	889	118

Table 15: Influence of Molding Conditions (Melt Temperature) on Shear Modulus (***G’*** , MPa) for Capron 8233G (Fiber-Glass Reinforced (Nylon 6, GF = 33 wt.%) at Various Test Temperatures

Melt Temp. (T_m), ^{0}C	Tested at - 40 ^{0}C	Tested at 23 ^{0}C	Tested at 120 ^{0}C
225	1,659	1,623	530
235	1,659	1,626	541
245	1,664	1,629	540
260	1,677	1,645	543
270	1,748	1,637	548
290	1,731	1,690	549
310	1,691	1,661	544

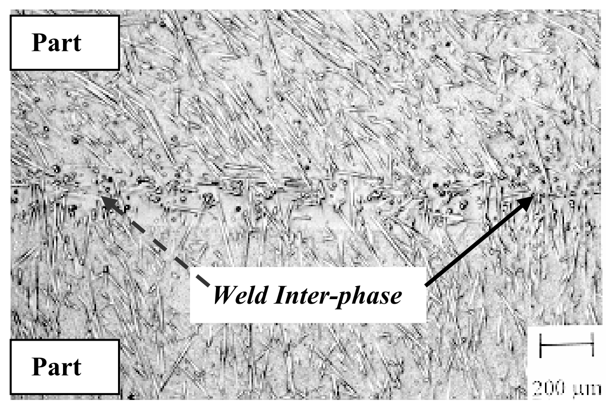

Figure 1: Local reinforcement effects at the weld inter-phase (a part of fibers are crossing the weld inter-phase)

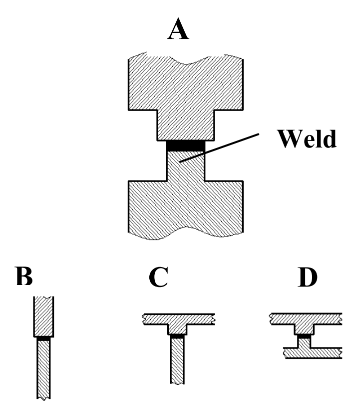

Figure 2: Welded joint design principles (types and configuration). Legend: A – joint design; B – butt joint (straight); C – butt joint (T – shape); D – shear / lap joint

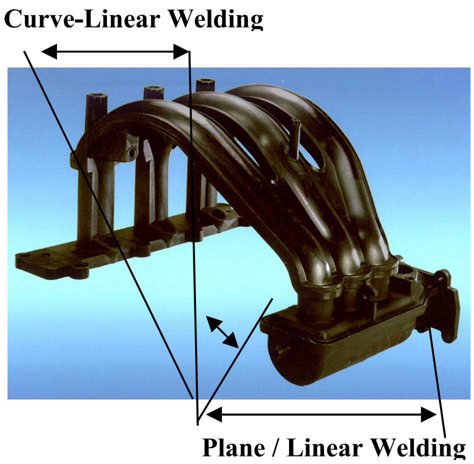

Figure 3: Linear Vibration Welded Plastic Air Intake Manifold (3 pieces)

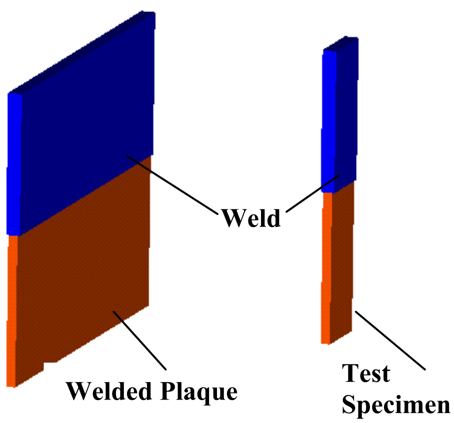

Figure 4: Model of welded straight butt joint (consists from two molded plaques welded together. Thickness of plaques is 6 mm and 4 mm) and machined / cut test specimen (width = 10 mm)

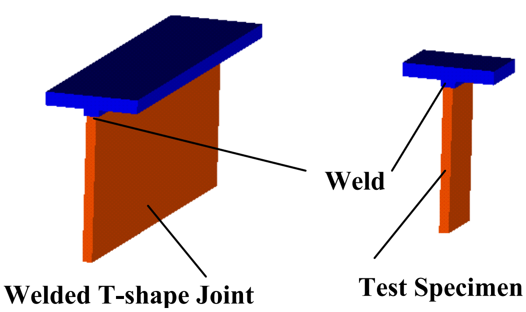

Figure 5: Model of welded T-shape butt joint (consists from welded together T-element and molded plaques. For T-element thickness of the weld bead is 6 mm. Thickness of the plaque is 4 mm) and machined / cut T-shape test specimen (width = 10 mm)

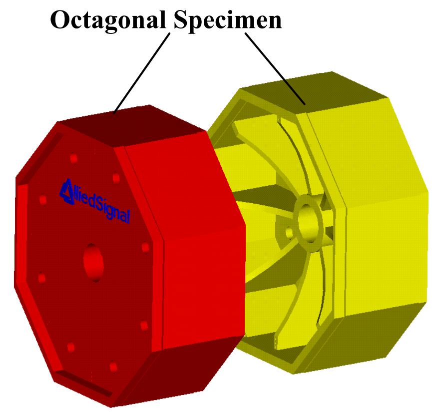

Figure 6: Multi-purpose universal welding & testing system (consists from welded together two octagonal specimens. Thickness of weld beads is: 6; 5; 4 and 2,5 mm)

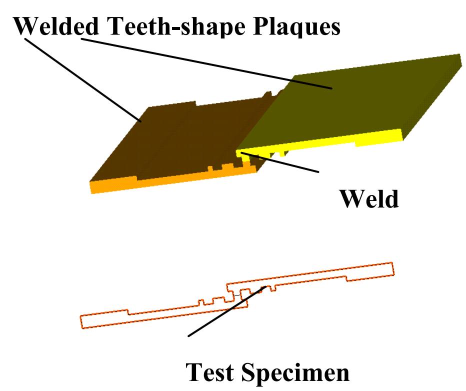

Figure 7: Model of welded shear / lap joint (consists from two teeth-shape injection molded plaques welded together. For teeth-element thickness of the weld beads are: 6; 4 and 2,5 mm)

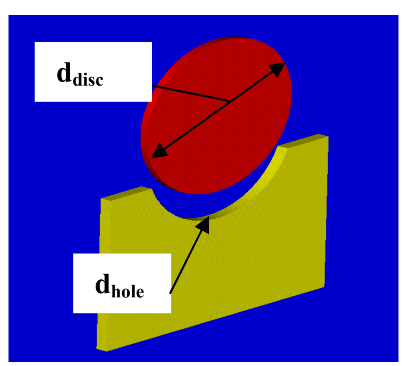

Figure 8: Curvilinear model of the welded joint (injection molded disc and plaque will be joined together by linear vibration welding)

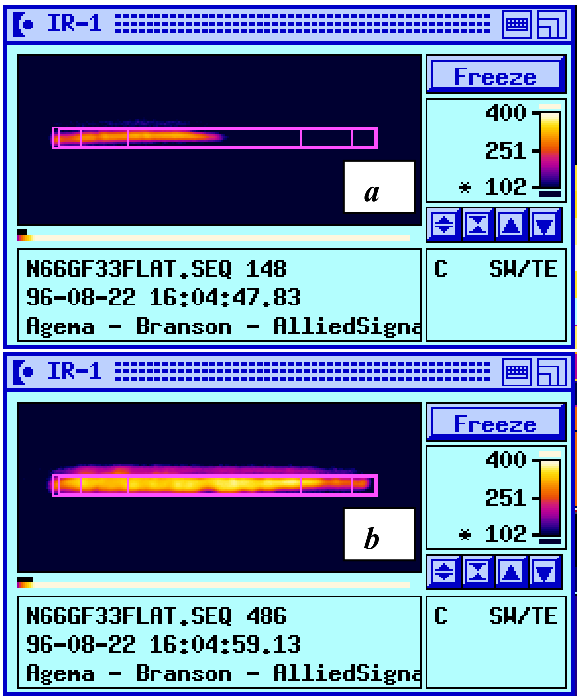

Figure 9: Temperature distribution in weld inter-phase (butt joint, nylon 66). ***a*** - heating initiation phase; ***b*** - at final phase of heating

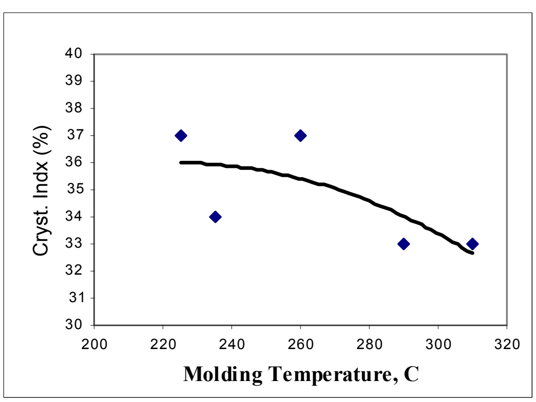

Figure 11: Influence of molding / melt temperatures on CI (crystallinity index)

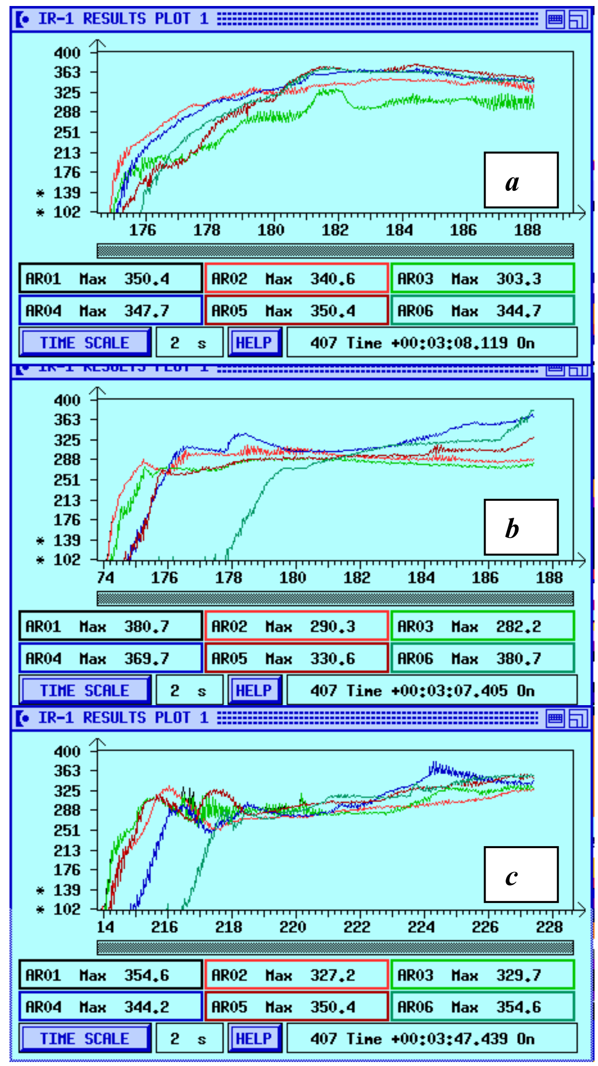

Figure 10: Time-temperature profiles (optimized LVW conditions, butt joint, and nylon 66). Type of plastics: ***a*** - - non-reinforced / non-filled; ***b*** - 33 wt.% fiberglass reinforced; ***c*** - fiberglass reinforced and mineral filled.

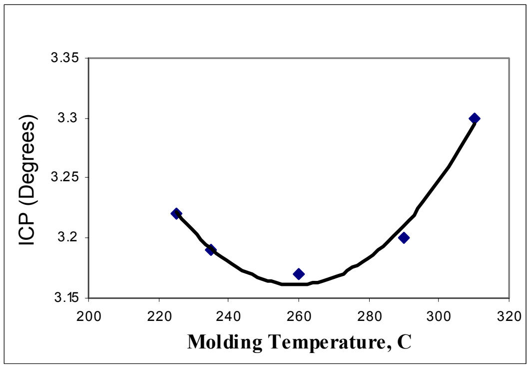

Figure 12: Influence of molding / melt temperatures on ICP

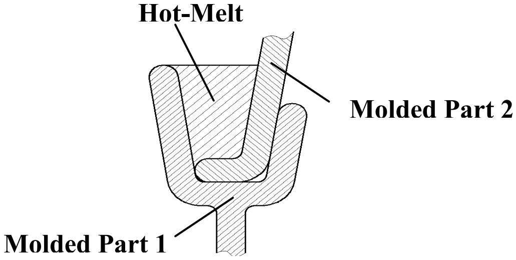

Figure 13: Principles of Hot-Melt joining (over-molding)

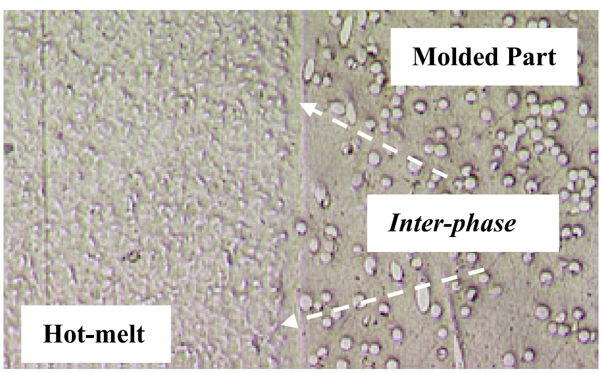

Figure 14: Joint Structure at Optimized Over-Molding Conditions

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

www.basf.com/usa
www.plasticsportal.com

HELPING MAKE PRODUCTS BETTER™

BASF