Influence of the Temperature Profile in the Interface on the Bond Strength of Polyamide–Polyurethane Two-Component Tensile Bars

G. Pompe, M. Bräuer, D. Schweikle, J. Nagel, B. Hupfer, D. Lehmann

Leibniz Institute of Polymer Research Dresden e.V., FRG-01005 Dresden, PF 12 04 11, Germany

ABSTRACT: Two-component tensile bars with polyamide 6 (PA) and thermoplastic polyurethane (TPU) unmodified and modified with 4,4'-diphenylmethane diisocyanate (MDI) have been investigated. It is known that the bond strength of PA/TPU tensile bars can increase by about 50% if MDI-modified polyurethane is applied. The subject of these studies is the analysis of the influence of the mass temperatures on the bond strength. The mass temperatures of the first and second injection process and the delay time between the first and second injection processes determine the temperature gradient in the interface at the moment of the second injection. There is an increase in the bond strength when there is an increasing temperature gradient; therefore, the mass temperature of the first component at the delay time has to be lower than the mass temperature of the second component. The temperature gradient can be used as a measure of the thermal annealing of the first component near the interface during the heat transfer from the second component. It can be concluded that effective thermal annealing causes an increase in the bond strength. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4297–4305, 2006

Key words: molding; polyamides; polyurethanes; processing; thermoplastics

INTRODUCTION

Good adhesion between the components plays an important role in the industrial application of multicomponent devices,[1,2] for which the combination of rigid and flexible components is of particular interest. For such studies, two-component (2C) tensile bars with polyamide 6 (PA) as the rigid component and thermoplastic polyurethane (TPU) as the flexible component are used, produced by an interface-reactive 2C injection-molding process.[3] The *in situ* chemical reaction between the amide and amino end groups of PA and the isocyanate (NCO) groups of TPU modified with 4,4'-diphenylmethane diisocyanate (MDI) has been applied to compatibilize both components during processing. The bond strength (σ_b) of 2C tensile bars with MDI-modified TPU increases by about 50% in comparison with that of 2C tensile bars produced with unmodified TPU.[4–7]

σ_b of composites is a very sensitive property, affected by the materials and also to a great extent by the processing conditions. Schweikle[7] investigated the influence of several processing conditions on σ_b of PA/

TPU tensile bars with unmodified and MDI-modified TPU. The following processing conditions were varied: the mold temperature, mass temperatures of the first component (PA) and second component (TPU C60D), delay time (t_{del}) between the first and second injection, injection velocity of both injections, specific holding pressure, and holding pressure time of the second injection. Both mass temperatures have a significant influence on σ_b. The aim of this article is a detailed analysis for determining the acting parameter responsible for the observed behavior. Because the technological, chemical, and polymer physical processes act together, a change in one processing parameter is usually connected to a change in different processes. For instance, the mass temperature influences the melt viscosity, recrystallization, interdiffusion, and chemical reactivity. From this point of view, an analysis can only obtain initial information on the most important parameter to be considered for processing PA/TPU tensile bars with high σ_b.

The influence of mass temperatures on σ_b can be summarized by only one responsible parameter—the temperature difference in the interface at the moment of the second injection. It must be taken into account that the temperature of the second component has to be higher than the temperature of the first injected component at the moment of the second injection.

Additionally, the influence of a changed order of injections on σ_b has been tested. The values of σ_b

obtained for one-interface PA/PA tensile bars are presented and discussed. The results confirm that a sufficient temperature gradient in the interface with increasing temperature from the first injected part to the second injected part is very important for a high degree of σ_b.

EXPERIMENTAL

Materials

PA (Ultramid B3K, BASF AG, Ludwigshafen, Germany) was used as the rigid component. This type is a stabilized variant of the PA6 products recommended for injection molding. The flexible component was TPU Elastollan C60D, a polyester urethane with a Shore D hardness of 60 (Elastogran GmbH, Lemförde, Germany).

The commercial designation used for the modifier MDI is Desmodur 44 M, a product from Bayer AG (Leverkusen, Germany).

The series of tests used for the special investigations was prepared with PA6 SH3 (Leuna Polymer GmbH, Leuna/Merseburg, Germany).

Processing

Modification of TPU

TPU was modified by reactive extrusion in a ZSK 30 corotating, twin-screw extruder (Werner & Pfleiderer, Stuttgart, Germany). The extruder had a length/diameter ratio of 41. A low-shear screw adapted for polyurethane thermoplastic processing was used. The machine was operated at a screw speed of 150 rpm.

TPU was dried before extrusion. The granules were fed gravimetrically with a total mass flow rate of 10 kg/h. MDI was fed gravimetrically or volumetrically in a molten state with a metering pump. The mass temperature increased from 175 to 220°C. The TPU melt strand was cooled, dried, and pelletized.

Unmodified and modified TPUs with 2 and 5 wt % MDI were used for the investigations presented in this article.

Injection-molding process

A 2C injection-molding machine (ES 200H/80V/50H HL-2F, Engel, Schwertberg, Austria) was used. The machine parameters were described by Hupfer et al.[4] 2C tensile bars of PA and TPU were produced in accordance with ISO 527 (type 1A). The granules were dried to a water concentration of less than 0.05% for PA and 0.02% for TPU before injection molding.

The injection-molding system was a core-back mold. The injection-molded test specimen (bar) was a 2C tensile test bar consisting of the hard component PA (first component) in the side parts and the soft

component TPU (second component) in the middle part produced by what is known as the core-back process. First, PA was injected from the horizontal injection units (gates a and b) at the PA mass temperature ($T_{PA} = T_{m,H} = T_{m,1}$) in the left and right parts of the mold with a movable core in the middle of the mold. The injection gate c of the vertical unit was located near one side of the core. After the cooling of the first component (PA) for a certain degree of solidification, the core was retracted out of the mold, and this opened the cavity for the second component (TPU), which was asymmetrically injected into the cavity at the TPU mass temperature [$T_{TPU} = T_{m,V} = T_{m,2}$; see Fig. 1(a)]. The relation $T_{m,V} < T_{m,H}$ was valid at the mass temperatures given in Table I. That means that the mass temperature of the second injected component (TPU) was lower than that of the first injected component (PA): $T_{m,2} < T_{m,1}$. The mold temperature of 60°C was unchanged.

For a special test, PA/PA tensile bars with only one interface with PA6 SH3 for both the horizontal and vertical injection units (gates a and b) were produced. A diagram of these PA/PA tensile bars is shown in Figure 1(b,c). t_{del} between both injection processes amounted to 20 s. Two bars were produced in the test series, in which the order was reversed (see Table II). For the V1/H2 tensile bar, the mass temperature of the second component with the horizontal unit (H2) was lower than the mass temperature of the first component with the vertical unit (V1). That means $T_{m,2} < T_{m,1}$. This ratio of the mass temperatures was analogous to the standard variant for processing PA/TPU tensile bars (see Table I).

The reversed order of the injections was used for processing the H1/V2 tensile bar. In this case, the mass temperature of the second component injected from the vertical unit (V2) was higher than that of the first component with the horizontal unit (H1). That means $T_{m,2} > T_{m,1}$. This was in contrast to the ratio of the mass temperatures of the V1/H2 tensile bar (Table II) and the PA/TPU tensile bars (Table I).

Methods of characterization

σ_b

σ_b was determined after storage under climatic conditions (23°C and 50% moisture) for 20 days. The water content of PA determined after this storage amounted to about 1%.

σ_b of the PA/TPU tensile bars was tested in accordance with ISO 527. The investigation of the influence of the tensile velocity on the strain–stress diagram led to the recommended tensile velocity of 50 mm/min[7] applied in the mechanical measurements. In each case, 10 PA/TPU tensile bars were tested. The values were average values. The scattering of the values in the
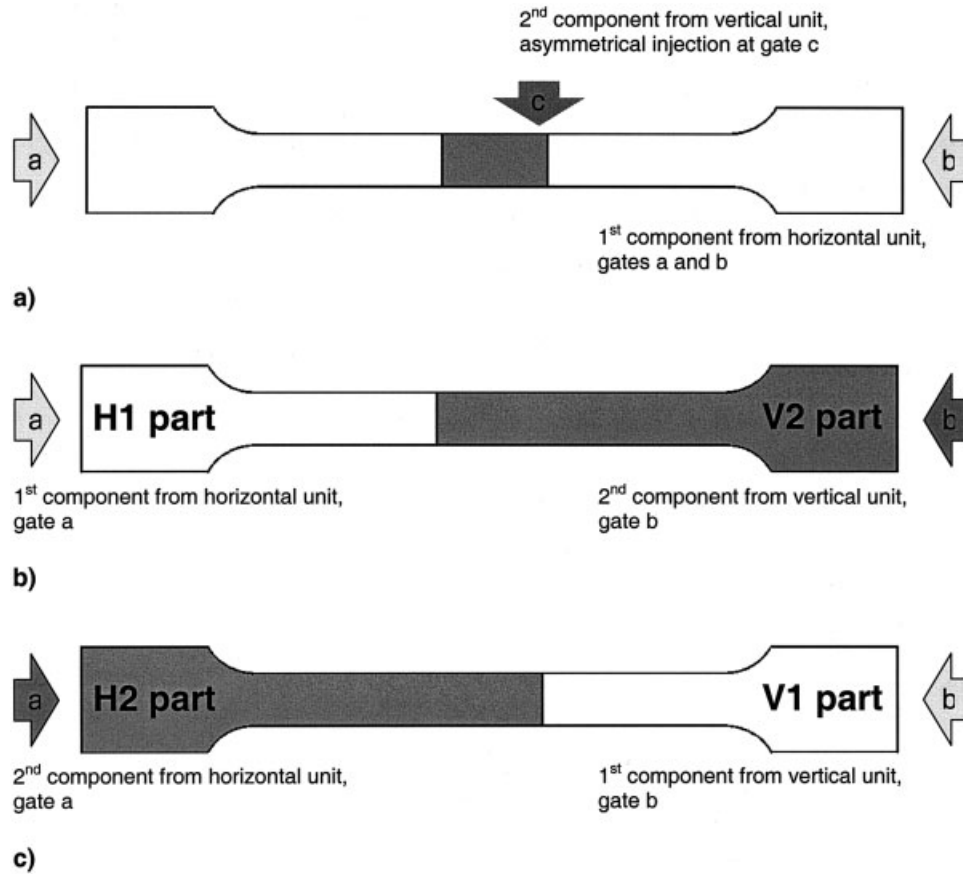
Figure 1 Scheme of (a) a 2C tensile bar with two interfaces and (b,c) a PA/PA tensile bar with one interface (the blank parts are the first component, and the dark parts are the second component).

series amounted to ±7%. The different behavior of the site of the fracture as a result of the asymmetrical injection of the second component in the mold [see Fig. 1(a)] had to be taken into account. A distinction

was necessary between the kinds of fractures with respect to the site of fracture. The description near the gate and away from the gate was used. Only when the fractures of almost all 10 PA/TPU tensile bars had taken place in the same interface was the average value suitable for a more detailed analysis. It is remarkable that the 2C tensile bars with TPU C60D analyzed in this article broke almost near the gate. Schweikle[7] observed a completely different behavior in the case of 2C tensile bars with polyurethane TPU C85A with Shore A hardness of 85. These 2C tensile bars with TPU of a low Shore hardness broke near the

TABLE I
Processing Parameters for the Injection Molding of PA/TPU Tensile Bars with Two Interfaces

Series	$T_{m,H} = T_{PA}$ (°C)[a]	t_{del} (s)	$T_{m,V} = T_{TPU}$ (°C)
01 (reference series)	*255*	*23*	*205*
02	*255*	**18**	*205*
03	*255*	**28**	*205*
04	**240**	*23*	*205*
05	**270**	*23*	*205*
06	**285**	*23*	*205*
07	*255*	*23*	**195**
08	*255*	*23*	**215**
09	*255*	*23*	**225**

The reference data are given in italics and the variable parameters are given in bold. The condition $T_{m,V} < T_{m,H}$ was as signed as the standard condition.
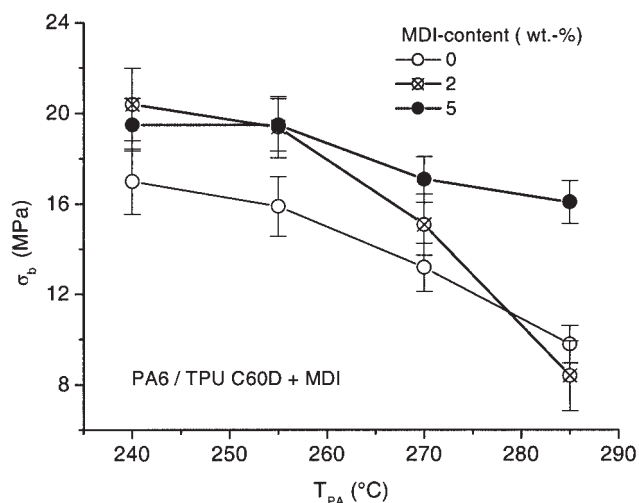
[a] The first component was PA6 B3K injected at $T_{m,H}$.

[b] The second component was TPU C60D (unmodified and MDI-modified) injected at $T_{m,V}$ ($<T_{m,H}$).

TABLE II
Mass Temperatures for the Injection Molding of PA/PA Tensile Bars with One Interface

	First-component PA		Second-component PA
V1/H2 tensile bar (standard conditions)	$T_{m,V} = 300°C$	>	$T_{m,H} = 270°C$
H1/V2 tensile bar	$T_{m,H} = 270°C$	<	$T_{m,V} = 300°C$

Figure 2 σ_b of PA/TPU tensile bars with unmodified and MDI-modified TPU C60D as a function of T_{PA} with the MDI content as a parameter.

gate and away from the gate in about equal amounts. Such average σ_b values are not suitable for a more detailed analysis.

The measurements of σ_b of the PA/PA tensile bars with one interface were taken analogously to those of the PA/TPU tensile bars. The value σ_b(V1/H2) could be determined only with a high inaccuracy of ± 9 MPa at an average value of 14 MPa ($\approx 60\%$), whereas the inaccuracy of σ_b(H1/V2) amounted to only ± 5 MPa at an average value of 64 MPa ($\approx 8\%$).

Differential scanning calorimetry (DSC)

The DSC investigations were conducted with a PerkinElmer (Wellesley, MA) DSC7 under a nitrogen atmosphere with the run cycle of first heating, cooling, and second heating. The temperatures and the melting heat were calibrated with In and Pb standards.

The DSC measurements of TPU were taken from -60 to $280°C$ at scanning rates of $+40$ and -10 K/min with a holding time of 0.5 min at a final temperature (T_{final}) of $280°C$. The recrystallization during the first heating in the melting range of the crystalline hard segments (HSs) of TPU[8] could be suppressed as far as possible with the high heating rate. This was important for a correlation of the thermal properties with the mechanical properties determined at room temperature. The samples were taken out of the middle of the TPU part by cutting. The mass of the TPU samples was about 10 mg.

For the PA/PA test series, the thermal behavior of PA near the interface was investigated. The samples were prepared as cuts of ≤ 1 mm thick and with a mass of about 8 mg and were measured within the temperature range of $10–250°C$ at scanning rates of

$+20$ and -10 K/min with a holding time of 0.5 min at $T_{final} = 250°C$. The heating rate of 20 K/min was chosen to reduce any recrystallization that might occur during the heating run. Although thinner samples would be more suitable for the characterization of the thermal behavior near the interface, the results already show interesting differences.

RESULTS AND DISCUSSION

Influence of the processing conditions on σ_b of the PA/TPU tensile bars

Almost all fractures of the investigated PA/TPU tensile bars occurred near the gate. The influence of T_{PA} (series 01 as a reference and series 04 to series 06) and T_{TPU} (series 01 as a reference and series 07 to series 09) on σ_b of the PA/TPU tensile bars is shown in Figures 2 and 3. Additionally, the effect of t_{del} on σ_b (series 01 to series 03) is plotted in Figure 4. With an increase in t_{del} from 18 to 23 s, there is an increase of about 8 MPa in σ_b. The further increase in t_{del} up to 28 s does not result in a further increase in σ_b.

The influence of both mass temperatures on σ_b is different. In general, σ_b decreases as T_{PA} increases (Fig. 2).

The variation in T_{TPU} results in differences in the behavior of unmodified and modified TPU (Fig. 3). In the case of unmodified TPU, no remarkable influence of T_{TPU} on σ_b can be observed. The values vary between 12 and 16 MPa. By comparison, σ_b of PA/TPU tensile bars with modified TPU increases from 14 MPa for $T_{TPU} = 195°C$ to 24 MPa for $T_{TPU} = 225°C$.

Although the qualitative behavior of σ_b as a function of T_{PA} and t_{del} is almost equal for both unmodified and modified TPU, the influence of T_{TPU} on σ_b
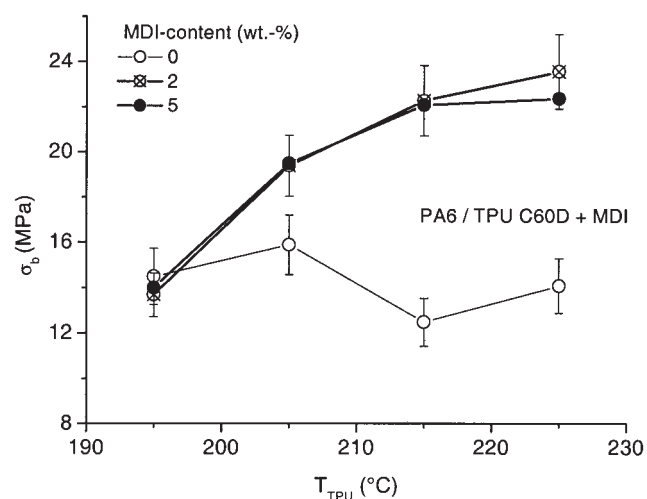
Figure 3 σ_b of PA/TPU tensile bars with unmodified and MDI-modified TPU C60D as a function of T_{TPU} with the MDI content as a parameter.
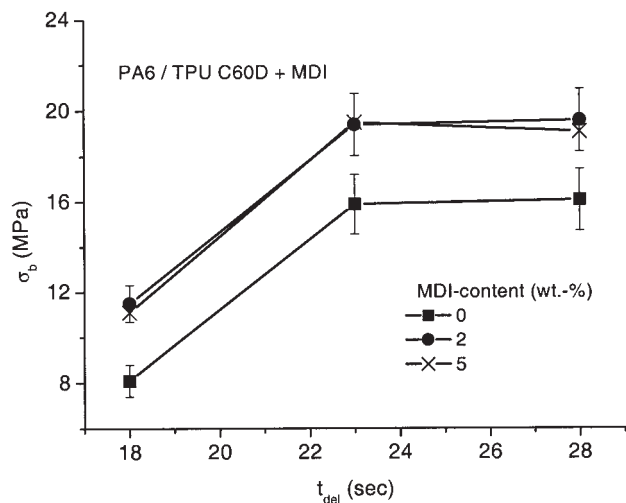
Figure 4 σ_b of PA/TPU tensile bars with unmodified and MDI-modified TPU C60D as a function of t_{del} between both injections with the MDI content as a parameter.

shows strong differences as a result of the modification. However, it is remarkable that the content of the modifier MDI (2 or 5 wt %) does not play a role in the series with various T_{TPU} and t_{del} values and with $T_{PA} < 270°C$ (Fig. 2). The difference between σ_b of PA/TPU tensile bars with 2 and 5 wt % modified TPU observed at $T_{PA} = 270°C$ increases as T_{PA} increases. The cause of this effect has not been investigated yet.

The results show that the change in T_{PA} and T_{TPU} has a different influence on σ_b. This different behavior can be understood if the mass temperature is considered in relation to the melting temperature of the respective component. For the PA component, all values of T_{PA} guarantee a complete melting of the PA crystallites and result only in an increase in the temperature of molten PA. It is possible that the observed decrease in σ_b may have been caused by a decreasing molecular weight of PA as a result of the increasing melt temperature.[9]

In the case of TPU, two effects must be taken into consideration. First, increasing T_{TPU} results in an increasing concentration in the reactive NCO groups.[5] Accordingly, the reactivity of the chemical reaction in the interface should increase connected with an increase in σ_b. Second, the increase in T_{TPU} from 195 to 225°C changes the morphology of the crystalline HS phase. Figure 5 shows how the melting behavior of the TPU was changed as a result of the MDI modification. The temperature range of the melting of HS crystallites in the unmodified TPU (140–230°C) is shifted to lower temperatures (110–200°C) as a result of the MDI modification. The content of the MDI does not play an important role. When modified TPU is used, almost all HS crystallites are molten for $T_{TPU} \geq 205°C$. In all other cases, a more or less partial melting of the HS crystallites takes place. For the residual nonmolten HS

crystallites, the processing is to a certain extent an annealing, connected to a change in the morphology of the HS crystallites. The thermal annealing causes an increase in the size of the HS crystallites connected with a stronger phase separation between soft-segment and HS phases. When the T_{TPU} values are near or above the upper end of the melting range, the effect of increasing phase separation disappears, and a good mixing state of the HS and soft-segment phases can be attained. The tensile strength of pure TPU correlates with the phase separation in TPU. The tensile strength decreases with increasing phase separation and increases with improved phase mixing.[10] Assuming that a similar influence on σ_b is possible, the following hypothesis is proposed: the varying influence of T_{TPU} on σ_b of the unmodified and modified TPU can be partially caused by the different manner of melting of the HS crystallites, in connection with a change in the phase mixing state of TPU and accordingly also with a change in σ_b of PA/TPU tensile bars.

Analysis of σ_b of the PA/TPU tensile bars as a function of the temperature behavior in the interface

The results obtained for the PA/TPU tensile bars with modified TPU presented in Figures 2 and 3 are analyzed from the point of view of the temperature behavior near the interface during processing. This analysis requires the temperature of the first injected component PA at the moment of the second injection, that is, after t_{del} [$T_{PA}(t_{del})$].

In the simple model used, the values are calculated as follows:
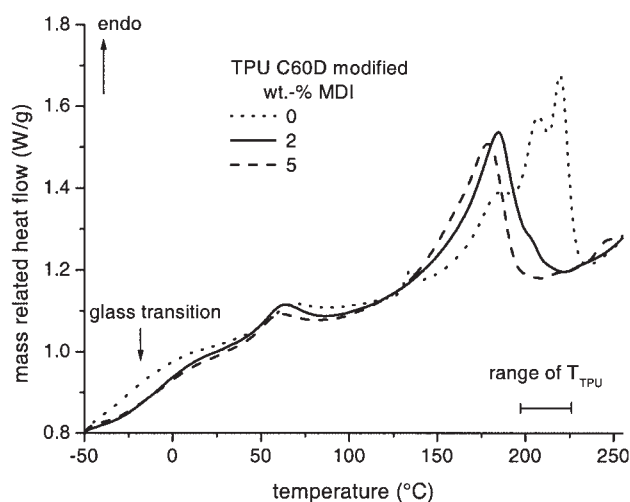
Figure 5 DSC scans of the first heating run of TPU C60D unmodified and modified with 2 and 5 wt % MDI (the samples were cut from the middle of the TPU part in series 01; heating rate = 40 K/min).
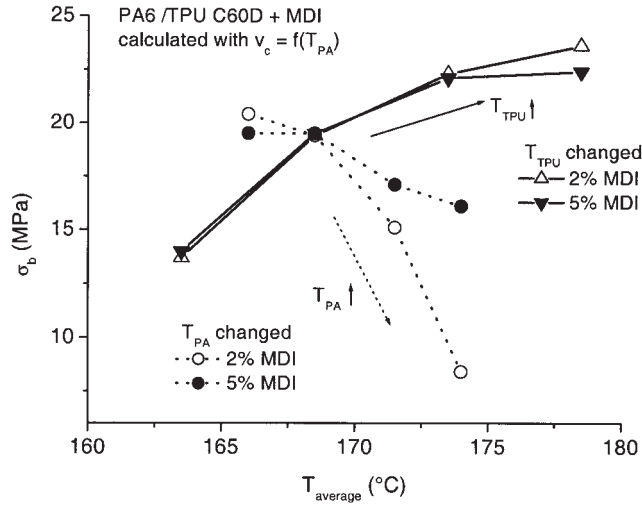
Figure 6 σ_b of PA/TPU tensile bars with MDI-modified TPU C60D as a function of $T_{\text{average}}(t_{\text{del}})$.

$$T_{PA}(t_{\text{del}}) = T_{PA}(1 - v_c t_{\text{del}}) \tag{1}$$

where v_c is the average cooling velocity of the material near the core in the mold (see the appendix). The cooling velocity is determined by the difference of the various PA mass and constant mold temperatures. The function $v_c(T_{PA})$, shown later in Figure A.1, has been used to calculate $T_{PA}(t_{\text{del}})$.

First, the dependence of σ_b on the so-called average temperature $T_{\text{average}}(t_{\text{del}})$, calculated by

$$T_{\text{average}}(t_{\text{del}}) = 1/2[T_{PA}(t_{\text{del}}) + T_{TPU}] \tag{2}$$

is discussed. $T_{\text{average}}(t_{\text{del}})$ describes more or less the temperature of a certain interphase right and left of the interface and should be a measure of the temperature at which the chemical reaction between both components takes place. The effectiveness of the chemical reaction as a thermally activated process should increase with $T_{\text{average}}(t_{\text{del}})$.

The σ_b values of PA/TPU tensile bars with modified TPU with varying T_{PA} and T_{TPU} and constant t_{del} (23 s) are plotted in Figure 6 as a function of $T_{\text{average}}(t_{\text{del}})$. No universal behavior of $\sigma_b = f[T_{\text{average}}(t_{\text{del}})]$ is found. σ_b increases if T_{TPU} increases and decreases if the increase in $T_{\text{average}}(t_{\text{del}})$ is caused by increasing T_{PA}. Apparently, the change in the reaction temperature [$\approx T_{\text{average}}(t_{\text{del}})$] as a result of the various mass temperatures in the range used does not play an important role in the improvement of σ_b.

Second, the influence of $\Delta T(t_{\text{del}})$ on σ_b is analyzed. The value, calculated by

$$\Delta T(t_{\text{del}}) = [T_{TPU} - T_{PA}(t_{\text{del}})] \tag{3}$$

is a measure of the temperature gradient between the TPU and PA parts near the interface. An increase in $\Delta T(t_{\text{del}})$ can be caused by both an increasing T_{TPU} and a decreasing T_{PA}. The function $\sigma_b = f[\Delta T(t_{\text{del}})]$ is shown in Figure 7. Regardless of the cause of the increase in $\Delta T(t_{\text{del}})$, σ_b always increases. It is remarkable that the behavior can be described practically by one function, $\sigma_b = f[\Delta T(t_{\text{del}})]$, regardless of whether the increase in ΔT is caused by an increase in T_{TPU} or by a decrease in T_{PA}. This result is an indication of the effect of thermal annealing on the increase in σ_b.

The estimation with a constant value of v_c (320 K/min) does not change the qualitative behavior neither for $\sigma_b = f[T_{\text{average}}(t_{\text{del}})]$ in Figure 6 nor for $\sigma_b = f[\Delta T(t_{\text{del}})]$ in Figure 7. The agreement of series with various T_{TPU} and T_{PA} values shown in Figure 7 is not as good as that in the calculation using $v_c(T_{PA})$.

The conclusion of the analysis is that an increase in σ_b of 2C tensile bars is possible if the condition $T_{PA}(t_{\text{del}}) < T_{TPU}$ or generalization $T_{m,1}(t_{\text{del}}) < T_{m,2}$ can be realized by the processing, for which $T_{m,1}(t_{\text{del}})$ should not be too low (in relation to the range of the various mass temperatures). It must be ensured that the transfer of heat from the second component to the first component will lead to a sufficient increase in the temperature of the first component near the interface to allow effective annealing.

Influence of the order of injections in the processing of the PA/PA tensile bars

The PA/PA tensile bars with one interface were prepared with the same polymer PA for the horizontal and vertical unit (see Table II).

The V1/H2 tensile bar [Fig. 1(c)] was produced with the vertical unit ($T_{m,V} = 300°C$) for the first injection
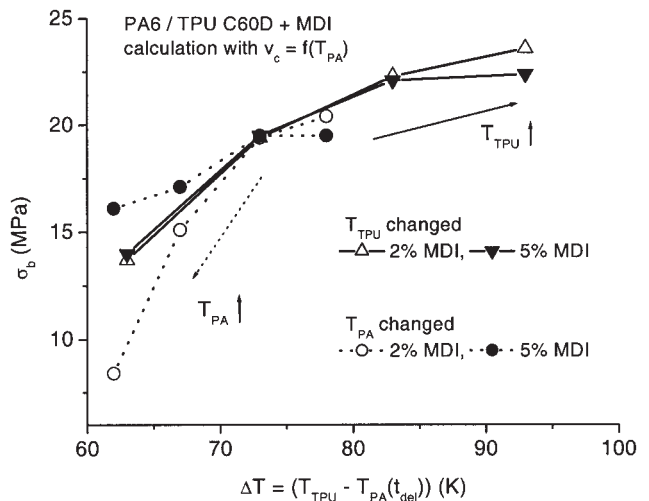
Figure 7 σ_b of PA/TPU tensile bars with MDI-modified TPU C60D as a function of $\Delta T(t_{\text{del}})$.
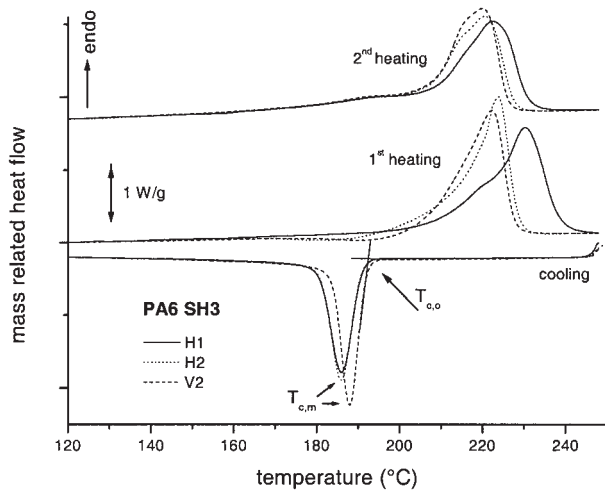
Figure 8 DSC scans of the first and second heating and cooling runs of PA samples cut near the interfaces of PA/PA tensile bars with one interface.

and the horizontal unit ($T_{m,H} = 270°C$) for the second injection. That means that the second component has a lower mass temperature than the first component ($T_{m,2} < T_{m,1}$), similarly to the condition in the standard processing of the PA/TPU tensile bars (Table I). σ_b of the V1/H2 tensile bars is very low and very uncertain: $\sigma_b(V1/H2) = (14 \pm 9)$ MPa.

σ_b of the H1/V2 tensile bars [Fig. 1(b)] with the reversed injection order and with $T_{m,2} > T_{m,1}$ amounts to $\sigma_b(H1/V2) = (64 \pm 5)$ MPa. This value is similar to the tensile strength of PA determined in an S2 bar of PA without an interface. The change in the injection order results in a significant change in σ_b by a factor of about 4. For the analysis of $\Delta T(t_{del})$ in the moment of the contact during the processing, eq. (3) can be written for the PA/PA test bars as $\Delta T(t_{del}) = [T_{m,2} - T_{m,1}(t_{del})]$. In the case of the V1/H2 test bar, the value amounts to about 95 K, and for the H1/V2 test bar, it is 145 K with the cooling velocity according to Figure A.1 (shown later) and the processing values for $T_{m,1}$, $T_{m,2}$, and $t_{del} = 20$ s (Table II). These results

confirm that an increasing value of $\Delta T(t_{del})$ is connected with an increasing value of σ_b (see Fig. 7).

The thermal behavior of PA near the interface was investigated with DSC for a more detailed analysis. Figure 8 shows the mass-related heat flow of the first and second heating and cooling runs for samples H1, H2, and V2 cut near the interface in each case. The values of the characteristic thermal properties of samples H1, H2, V1, and V2 are given in Table III. The thermal behavior described in the first heating scan has to be analyzed for the discussion in relation to σ_b. Special attention is given to the small exothermic effects in the first heating scan in the temperature range from 160 to 200°C. The exothermic effect points to the so-called cold crystallization of residual crystallizable PA taking place as a result of the thermal treatment during the first heating run. This effect is only possible if PA is not completely crystallized during the processing. Such behavior has also been found in many further DSC measurements of PA cuts near the interface of PA/TPU tensile bars. The H1 sample (see Fig. 8) is the only known exception in that regard. That means that only under the processing conditions used for the H1/V2 tensile bar crystallization during processing of the crystallizable PA of the first component near the interface (H1) is possible.

As a result of the molten state of PA at $T_{final} = 250°C$ of the first heating run, the material's thermal history, which influences its crystallinity, is cancelled. The similar crystallization behavior of the H1 and H2 samples in the cooling scans (Fig. 8) shows that the order of processing does not influence that aspect. The differences between the crystallization behavior of the H and V samples were explained by the greater reduction in the molecular weight of PA as a result of the higher value of $T_{m,V}$ (300°C) with the vertical unit in comparison with $T_{m,H}$ (270°C) at the injection with the horizontal unit. The influence of a changed molecular weight can be better observed by the crystallization as a kinetic process than by the melting process.

It can be summarized that the most interesting effect of the thermal behavior in connection with the analy-

TABLE III
Characteristic Thermal Properties of the PA Samples: Cuts from PA/PA Tensile Bars

PA sample	First heating (20 K/min)		Cooling (10 K/min)				Second heating (20 K/min)
	ΔH (150–240°C; J/g)	T_m (°C)	ΔH_c (150–200°C; J/g)	$T_{c,o}$ (°C)	ΔT_c (K)		T_m (°C)
H1	78	230.4	−69.5	191.0	4.9		222.5
H2	68	223.9	−69.8	190.7	4.8		220.5
V1	66	223.6	−71.7	192.6	4.2		221.5
V2	64	222.3	−71.7	191.9	4.0		220.0

ΔH = melting heat as determined in the temperature range 150–240°C; T_m = peak temperature of endothermic melting; ΔH_c = crystallization heat as determined in the temperature range 150–200°C; $T_{c,o}$ = extrapolated onset temperature of crystallization (see Fig. 6); $T_{c,m}$ = peak temperature of crystallization; $\Delta T_c = T_{c,o} - T_{c,m}$.

sis of σ_b is the absence of the cold-crystallization effect in the first heating scan of the H1 sample. This effect is explained by means of the following hypothesis: the H1 sample is the PA part near the interface that is injected first. Apparently, the transfer of heat from the second PA component (V2 part) injected with $T_{m,V}$ = 300°C to PA of the first injection (H1 part) is sufficient to heat the PA part near the interface (sample H1) to temperatures at which effective thermal annealing is possible. Consequently, all crystallizable PA in the H1 sample can be crystallized during the processing, and no cold-crystallization process can be observed in the first heating scan. The high value σ_b(H1/V2) = 64 MPa shows that the best σ_b value is achieved in this case. This means that both PA parts have very good contact in the interface of the H1/V2 tensile bar. It must be emphasized that the absence of the cold crystallization is only a sign of effective thermal annealing. The improvement of contact in the interface can be caused not only by the cold crystallization and partial melting with subsequent recrystallization but also by the interdiffusion of PA molecules across the interface.

In connection with the results of this special test series, the investigations on PA/TPU tensile bars published by Hupfer et al.[4] should be mentioned. The authors also reversed the order of the injections. σ_b in all samples in which the second component was injected with the higher mass temperature was up to 3 times higher than that in the samples with the reverse injection order. This effect was observed for PA/TPU tensile bars with both two interfaces [Fig. 1(a)] and one interface [Fig. 1(b,c)].

To summarize, the conclusion can be drawn again that a certain thermal annealing of the part near the interface of the component injected first causes an increase in σ_b.

CONCLUSIONS

The σ_b values of PA/TPU tensile bars with polyurethane with Shore D hardness have been discussed as a function of the mass temperatures. The influence of T_{TPU} is very important but also very complex. The effect of T_{TPU} can be understood only in relation to the melting behavior of TPU. Higher values of σ_b of PA/TPU tensile bars were obtained when almost all HS crystallites were molten during processing. In this case, the phase separation of the HS and soft segment of TPU after processing is not very significant. Good phase mixing in TPU appears to be conducive to a high σ_b value in the PA/TPU tensile bars. Consequently, it is recommendable to know the melting behavior of the TPU type to establish a suitable T_{TPU} value.

It has also been observed that a high σ_b value of 2C tensile bars can be obtained if the temperature of the

second component is higher than that of the solidified first component after t_{del}. σ_b increases as the temperature difference increases. Besides, the temperature of the solidified first component after t_{del} should not be too low. The increase in the temperature of the first injected component near the interface during heat transfer from the second component must be sufficient to permit an effective annealing of the interface region.

A very high value of σ_b was observed in the case of PA/PA tensile bars produced with a high temperature difference. This σ_b value was close to the tensile strength of PA. The optimum value of the mass temperature difference at the moment of the second injection favorable for high values of σ_b is dependent on the material combination used for the 2C devices. The materials and their melting temperatures also determine the injection order. A remelting of the first component in the bulk has to be avoided to obtain good dimensional stability. With current technology, it is not possible to inject the TPU component for PA/TPU devices first. In this case, the temperature difference in the interface at the moment of the second injection is limited, and accordingly the attainable σ_b value is limited too.

A further understanding of the thermal processes at the interface may help in developing advanced technologies for the production of 2C devices with high σ_b values.

APPENDIX: COOLING VELOCITY—PARAMETER CHARACTERIZING THE COOLING BEHAVIOR OF PA AS THE FIRST INJECTED COMPONENT

The cooling behavior of the injected mass at the core, necessary for the 2C injection process, is determined by a nonstationary heat-transfer process. A simple model for the approximation of $T_{PA}(t_{del})$ is applied to characterize the cooling behavior of the PA part near the interface. This model uses v_c, which is dependent on the difference between T_{PA} and the core temperature.

In an experimental attempt, an infrared-sensitive thermometer was fixed on the mold wall. With the temperature–time function, v_c was estimated with

$$v_c = [T_{PA}(t = 0) - T_{PA}(t_{del})]/t_{del} \qquad (A.1)$$

to be about 500 K/min for t_{del} = 23 s.

However, the core is not fully connected thermally with the mold, and accordingly the temperature of the core should be higher than that of the mold. Consequently, the cooling velocity for the PA part near the core should be lower than 500 K/min.
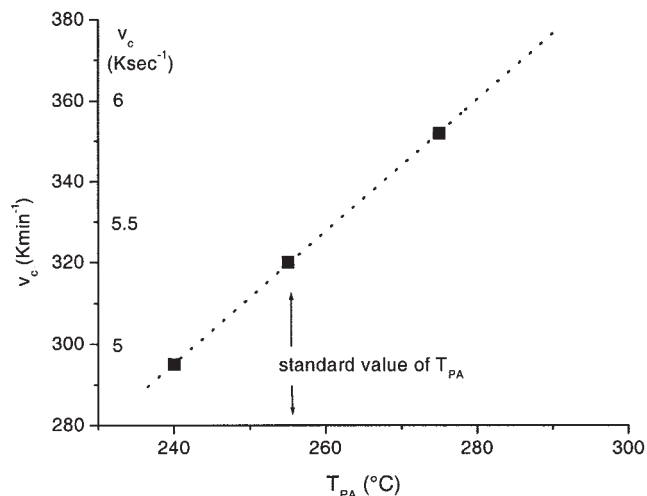
Figure A.1 v_c of the injected mass near the core in the mold as a function of the mass temperature of the first injected component (T_{PA}).

Schweikle[7] estimated $T_{PA}(t_{del} = 23$ s) for the 2C injection process at various T_{PA} values (240, 255, and 275°C) under the assumption of a nonstationary heat-transfer process.[11] With the calculated values $T_{PA}(t_{del} = 23$ s)[7] and eq. (A.1), the v_c values have been estimated and plotted in Figure A.1 as a function of T_{PA}.

The value $v_c = 320$ K/min obtained for the standard condition ($T_{PA} = 255°C$) seems to be a good approximate value for the cooling process near the core. A linear dependence, $v_c = f(T_{PA})$, can be assumed in the limited range of T_{PA} and for $t_{del} \leq 23$ s. This function $v_c = f(T_{PA})$ is used to analyze σ_b with respect to the mass temperatures with T_{PA} varying from 240 to 285°C.

References

1. Jaroschek, C.; Pfleger, W. Kunststoffe 1994, 84, 705.
2. Kuhmann, K. Kunststoffe 2001, 91, 115.
3. Lehmann, D.; Hupfer, B.; Bräuer, M.; Reinhardt, G.; Schweikle, D. Ger. Pat. DE-PS 198 10 312 C 2 (1998/2000).
4. Hupfer, B.; Lehmann, D.; Reinhardt, G. Kunststoffberater 1998, 10, 41.
5. Bräuer, M.; Hupfer, B.; Nagel, J.; Lehmann, D. Polym Eng Sci 2002, 42, 859.
6. Nagel, J.; Bräuer, M.; Hupfer, B.; Lehmann, D.; Lunkwitz, K. Kautsch Gummi Kunstst 2004, 57, 240.
7. Schweikle, D. Diploma, Fachhochschule Aalen and Institut für Polymerforschung Dresden, 1999.
8. Van Bogart, J. W. C.; Gibson, P. E.; Cooper, S. L. J Polym Sci Polym Phys Ed 1983, 21, 65.
9. Becker, G. W.; Braun, D.; In Polyamide, Kunststuffhandbuch Ed.; Hanserverlag: Munich, 1998; Vol. 3/4, Chapter 2.3.
10. Pompe, G.; Pötschke, P.; Pohlers, A.; Pionteck, J. Polymer 1998, 39, 5147.
11. Handbuch der Temperierung mittels flüssiger Medien; Hüthing-Verlag: St. Gallen, Switzerland, 2003; Vol. 11.