

Toughness Optimization of Glass-Fiber Reinforced PA 6/PA 66-Based Composites: Effect of Matrix Composition and Colorants

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ABSTRACT: Mixing of polyamide 6 (PA 6) and polyamide 66 (PA 66) is integrated in the trend of development of new and improved materials by combination of different polymers and some reinforcing materials to polymer composites. The specific polymer composite PA 6/PA 66 reinforced with short glass-fibers combines the good coloring of PA 6, and the small moisture absorption of PA 66. Technical applications of PA 6/PA 66 composites are mainly used in the automotive industry. Specific requirements of this industry lead to the necessity to optimize the material resistance against crack propagation of the PA 6/PA 66 composites, using mechanical and fracture mechanical methods. So, the present investigations focus on fracture mechanics toughness optimization of the PA 6/PA 66 composites, including unstable and stable crack growth. The aim of this toughness optimization is to find out the

optimal mixing ratio of PA 6/PA 66. Applications of PA 6/PA 66 in the automotive industry and specific client wishes are the main reasons for black-coloring of the PA materials. The influence of several black-colorants (carbon black, nigrosine, spinel, iron oxide) on mechanical and fracture mechanical properties of the PA composites is also investigated using fracture mechanical methods. As experimental fracture mechanical method, preferentially, the instrumented Charpy impact test (ICIT) and the new cut method to determine the stable crack growth of glass-fiber reinforced materials was used. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2245–2252, 2009

Key words: polyamide 6/polyamide 66 composite; colorant; crack resistance curve; fracture mechanics; instrumented Charpy impact test (ICIT); cut method

INTRODUCTION

Polyamides (PA) belong to the class of technical polymers, in which they are the most used ones. In the past 10 years, the world-wide PA usage is increased by about 7% per year and there is no end for this development.

PA, and their blends and composites, are mainly used in the automotive industry, for example as bleed air taps, tank flaps, fuel distributors, or engine dust covers. These partially safety relevant automotive components require specific properties of the used materials, in consideration of mechanical and fracture mechanical values. For this reason, a toughness optimization of the used PA materials is essen-

tial, including unstable and stable crack growth behavior.¹

Because of the specific applications of PA in the automotive industry, the PA became black in color. Black is the dominant color in the automotive industry,² and thus it is a basic requirement for the successful commercialization of the product. So it is necessary to investigate the influence of the black colorants on the toughness behavior of the PA materials.

Possibilities of toughness optimization of PA materials by blending with elastomers or thermoplastics, and reinforcing with particles or fibers are described in the literature.^{1,3–6} Especially fiber-reinforced composites have a wide range of applications in the plastics industry, because of their positive mechanical properties.

The specific PA 6/PA 66 based composite investigated in this study combines the favorable toughness properties as well as the good coloring of PA 6 and the small moisture absorption of PA 66 as published elsewhere.⁷ In addition to these engineering properties, PA 6/PA 66 blends are characterized by

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a typical crystallization behavior. Starting from pure PA 6, the PA 6 crystallization temperature increases slightly with increasing PA 66 content up to about 30 wt %. For PA 66 contents more than 30 wt %, the PA 6-crystallization temperature decreases. This retarded decreasing of the PA 6 crystallization temperature is caused by a structural and a thermal effect during melt crystallization. The symmetric PA 66 (symmetric molecular architecture) crystallizes at higher temperatures, and consequently, faster than the unsymmetric PA 6. In this case, the already crystallized PA 66 is used as nucleating agent for PA 6. This fact explains that the crystallinity of PA 6 is higher in the PA 6/PA 66 blend than in pure PA 6.^{8,9}

The PA 6/PA 66 blends show a characteristic, spherulitic morphology.^{8,9} In many cases, a post-crystallization of PA 6 in the gaps of the PA 66 spherulites can be observed. Furthermore, the crystal-crystal phase transition in PA 66 is known as Brill transition. A crystal modification from triclinic to pseudo-hexagonal of the PA 66 crystalline phase can be achieved, with annealing in the range of about 443 K ("Brill transition temperature").¹⁰ This modification results in an increased crystallinity, and consequently increased strength and stiffness, respectively.

Within the amorphous phase of the PA 6/PA 66 blends, a good compatibility between PA 6 and PA 66 can be observed.¹¹

In this study, it is focused on fracture mechanics toughness optimization of the PA 6/PA 66 based composites, such as unstable and stable crack growth. The aim of this toughness optimization is to find out the optimal mixing ratio of PA 6/PA 66. Furthermore, the influence of several black-colorants is investigated.

EXPERIMENTAL

Materials

Subject of the investigations were blends of PA 6 and PA 66 reinforced with 30 wt % short glass-fibers (herein after referred to as "PA 6/PA 66 composites"), provided by BASF-Leuna GmbH. Composites with different mixing ratios of PA 6 and PA 66 (100/0, 75/25, 50/50, 25/75, 0/100) were used. To investigate the influence of colorants on mechanical properties of the PA composites, the 50/50-composite was colored with carbon black, nigrosine, spinel, and iron oxide, respectively.

The polymers and the added short glass-fibers were blended in a double screw extruder, and afterwards the specimens were prepared by injection molding. The initial length of the short glass-fibers was 2 mm, and the final length of the fibers was 200

µm after injection molding. Note that these are average values of the distribution of the short glass-fibers.

The investigations exclusively took place in the moisture-free condition state.

Instrumentation

Basic characterization

Analysis of the thermal behavior of the PA 6/PA 66 composites was carried out by differential scanning calorimetry (DSC), following standard ISO 11357-1.¹² The mechanical properties were investigated by tensile test, in accordance with the standard ISO 527-1.¹³ The hardness of the PA composites was acquired using ball indentation test, in accordance with the standard ISO 2039-1.¹⁴

Toughness characterization

In addition to conventional investigations of the toughness behavior using Charpy impact test (CIT), according to standard ISO 179-1,¹⁵ fracture mechanics investigations, using the instrumented Charpy impact test (ICIT), were carried out. In the second case, the "procedure for determining the crack resistance behavior by instrumented Charpy impact test"¹⁶ developed at the Institute of Material Science was used. Using ICIT, the process of unstable and stable crack growth, respectively, was included for the characterization of the toughness behavior.

To determine fracture mechanics values as resistance against *unstable* crack growth, single-edge-notched bend (SENB) specimens (dimensions 4 × 10 × 80 mm³), with an initial crack were used. The initial crack has a length of 2 mm (initial crack length/specimen width; $a/W = 0.2$), and was created by a razor blade. The fracture mechanics value J_{Id} was determined using the J -integral-concept. Using the recommendation of SUMPTER and TURNER described in Ref. 16, the total deformation energy (A_G) was splitted in an elastic part (A_{el}) and in a plastic part (A_{pl}) [eq. (1)].

$$J_{Id} = \eta_{el} \frac{A_{el}}{B(W-a)} + \eta_{pl} \frac{A_{pl}}{B(W-a)} \frac{W - a_{eff}}{W - a} \quad (1)$$

where η_{el} and η_{pl} are the geometrical functions, B is the specimen thickness, W is the specimen width, a is the initial crack length, and a_{eff} is the effective crack length.

To determine fracture mechanics values as resistance against *stable* crack growth, single-edge-notched bend specimens were also used. The actual initial crack has a length of 4.5 mm (initial crack length/specimen width; $a/W = 0.45$).

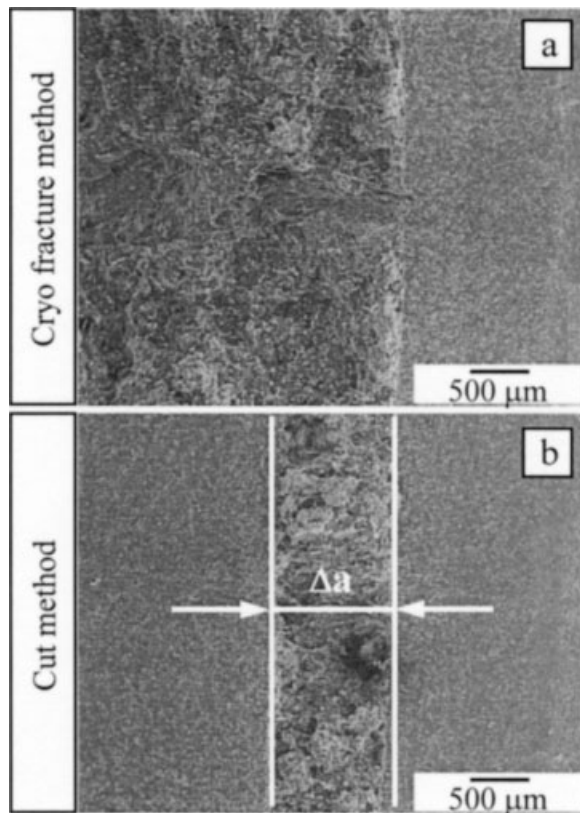


Figure 1 SEM images of stable crack growth areas, using cryo fracture method (top, a), and cut method (bottom, b), of uncolored PA 6/PA 66 (50/50).

Crack resistance curves were recorded by stop-block-method is described in the literature.^{17,18} Using this method, restricted specimen deflections were realized by a device for catching the impact pendulum (so-called stop-block), with a defined adjustable deflection. The different specimen deflections lead to different stable crack growths Δa . The stable crack growth Δa was placed in a diagram as a function of the associated J values. A curve fitting results in a characteristic crack resistance curve. The usage of the concepts of elastic-plastic fracture mechanics allows the determination of the tearing modulus T_J as fracture mechanics value. This value was calculated with the slope of the crack resistance curve, combined with the dynamic flexural modulus in relation to the squared dynamic yield stress [eq. (2)].

$$T_J = \frac{dJ}{d(\Delta a)} \frac{E_d}{\sigma_d^2} \quad (2)$$

where E_d is the dynamic flexural modulus and σ_d is the yield stress determined from ICIT under dynamic loading.

The classic proceeding to determine the stable crack growth Δa is the so-called cryo-fracture method. Using this method, the specimens with dif-

ferent stable crack growths Δa was separated by an impact pendulum, after storage in the liquid nitrogen. So, an unstable crack growth was created, in addition to the stable crack growth. Now, it is possible to differentiate optical between unstable and stable crack growth processes.

In most cases, the cryo-fracture method has the disadvantage, that it is impossible to measure the stable crack growth Δa of glass-fiber reinforced materials, using scanning electron microscope (SEM), shown in Figure 1(a) (top). The reason for this impossible measurement is the big similarity of the fracture surfaces of unstable and stable crack growth process. Both fracture surfaces are so cliffy that an optic differentiation of the two crack growth processes is not possible. To equalize this disadvantage, the new cut method was developed in the present study and described in detail in the literature.¹⁹ Using the new cut method, the specimens with different stable crack growths Δa were clamped in a specific in-house cutting device. Now, the clamped samples were separated in such a manner that a very thin metal blade cuts the specimen at the opposite site of the notch in direction to the notch. So, the rest ligament, i.e. the part of the specimen, which is not broken after applying a defined stable crack growth was cutted by a thin metal blade. The cut method has to be prepared such that no additional stresses occur during the move of the metal blade through the rest ligament. Figure 1(b) (bottom) shows the SEM image of a PA composite after separating with the cut method. Now, the stable crack growth Δa can be estimated clearly. Only with the cut method, it is possible to determine the stable crack growth of glass-fiber reinforced materials.

RESULTS AND DISCUSSION

Influence of the weight fraction of PA 66

Basic characterization

The mixing ratios between PA 6/PA 66 25/75 and PA 6/PA 66 75/25 are characterized by typical crystallization effects. In agreement with former research,^{8,9} the actually DSC measurements show an increase of the PA 6-crystallization temperature, with increasing PA 66 content up to about 25–50 wt % PA 66 (Table I). This is a specific effect based on the interactions between fastly crystallized PA 66, and resultant nucleation effect of PA 66 on PA 6, is explained in detail in the introduction part.

The mechanical properties of the faster crystallized PA 66 phase dominated for PA 66 contents more than 50 wt %, as it is shown by results of the tensile test (compare Table I). The determined tensile strength is approximately on the same level for PA 66 contents up to 50 wt %, because of the main

TABLE I
Basic Characterization: Some Mechanical and Thermal Properties of Uncolored PA Composites

PA 6/PA 66 (wt %)	DSC		Tensile test	Ball indentation test
	T_c (PA 6) (K)	T_c (PA 66) (K)	σ_M (MPa)	H (N/mm ²)
100/0	461	–	184 ± 1	172 ± 8
75/25	473	489	181 ± 1	157 ± 8
50/50	466	494	180 ± 2	158 ± 6
25/75	454	500	185 ± 1	165 ± 9
0/100	–	508	195 ± 1	185 ± 5

influence of the PA 6 phase, which was crystallized on the already crystallized PA 66. The influence of the PA 6 phase becomes smaller, and results in a slightly increase of the tensile strength for PA 66 contents more than 50 wt %.

Table I also shows the results of the ball indentation test. There is a maximum of hardness for both pure PA polymers, and a minimum for 75/25 and 50/50 mixing ratios. The lower hardness values can be explained by mutual damage of crystallization of the two involved blend phases, PA 6 and PA 66.⁷

Toughness characterization

Figure 2 shows the load-deflection behavior of the investigated PA composites with different mixing ratios. All PA composites investigated exhibit dominantly unstable crack growth behavior, at specific experimental conditions: $a/W = 0.2$ (black-filled curves). The unstable crack growth behavior is characterized by a typical strong decrease of the load. To

evaluate the stable crack growth behavior, the experimental conditions have to be changed to $a/W = 0.45$ (gray-filled curve). The stable crack growth behavior is characterized by a gradually decreasing of the load, and the presence of crack propagation energy A_R . The maximum load and the maximum deflection decrease, with increasing PA 66 content, for the unstable crack growth process and even more for the stable crack growth process. In both cases, the area under the load-deflection curves up to F_{max} , which corresponds to the general deformation energy A_G decreases with increasing PA 66 content. This fact reveals energy-determined crack growth behavior.

Figure 3 shows the standardized toughness values, J_{Id} (filled triangles) and a_{cN} (filled squares), as a function of PA 66 content. The resistance against unstable crack growth J_{Id} decreases with increasing PA 66 content by about 26%. In contrast to this, the classical determined Charpy impact toughness values a_{cN} only show a reduction by about 7% with

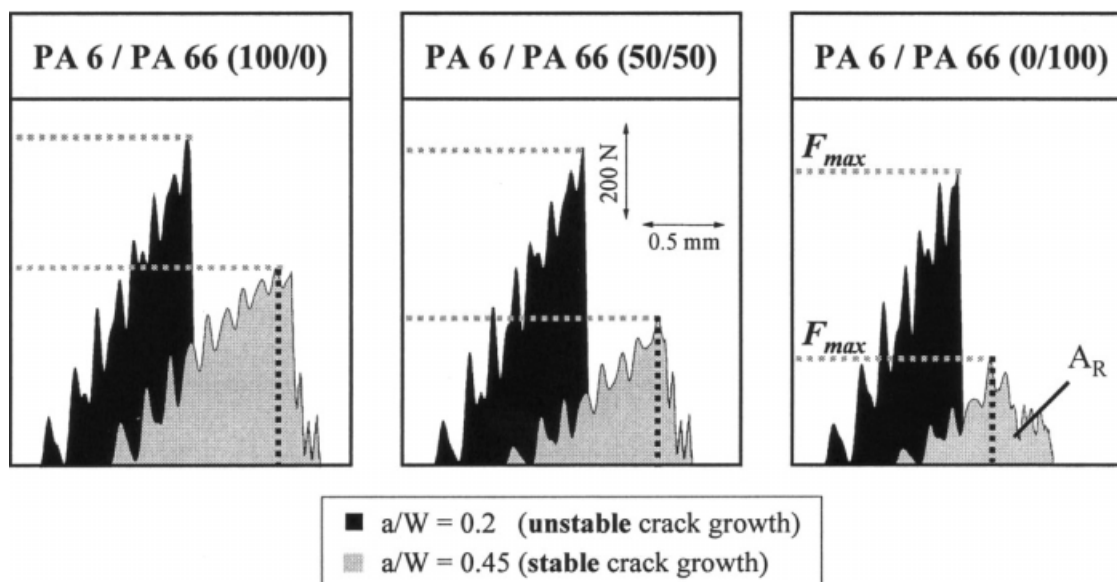


Figure 2 Load-deflection behavior of the investigated PA composites, with different PA 6/PA 66 mixing ratios: 100/0 (left), 50/50 (center), 0/100 (right).

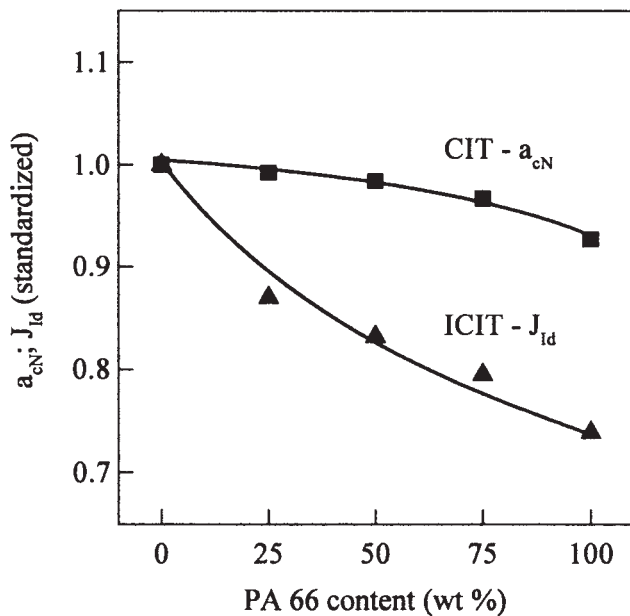


Figure 3 Resistance against unstable crack growth J_{Id} , and CHARPY impact toughness a_{cN} , as a function of PA 66 content.

increasing PA 66 content. It can be stated that the resistance against unstable crack growth J_{Id} clearly characterizes the existing toughness deficit.

The resistance against stable crack growth is evaluated using crack resistance curves. Three crack resistance curves are shown exemplary in Figure 4, representing pure PA 6, the 50/50 composite, and pure PA 66. A slight reduction of the slope of the

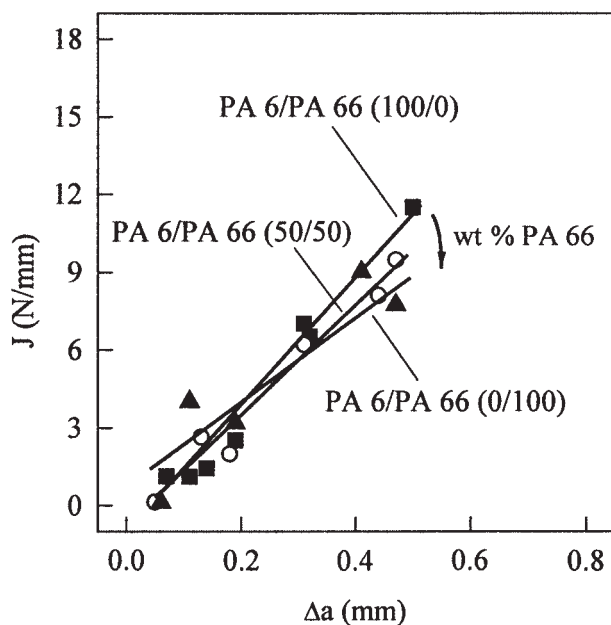


Figure 4 Crack resistance curves of the investigated PA composites with different PA 6/PA 66 mixing ratios: 100/0 (filled squares), 50/50 (open circles), 0/100 (filled triangles).

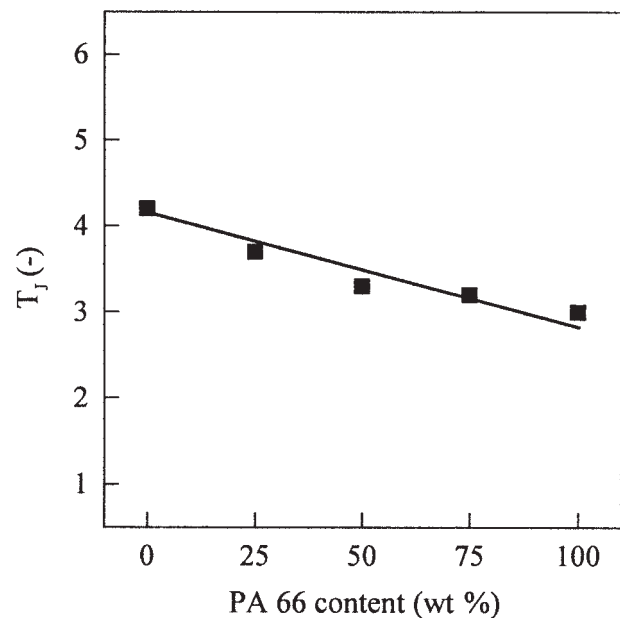


Figure 5 Resistance against stable crack initiation and propagation T_J (tearing modulus) as a function of PA 66 content.

curves can be observed with increasing PA 66 content. Figure 5 is a plot of the tearing modulus T_J , i.e., of the resistance against crack propagation as a function of PA 66 content. The resistance against crack propagation decreases, with increasing PA 66 content by about 28%. Figure 6 shows SEM images of pure PA 6 (top, left image), 50/50 composite (top, right image), and pure PA 66 (bottom). The images show the fracture surface morphology of the PA composites after stable crack growth. The reduction of the toughness, i.e., the resistance against stable crack propagation, can be illustrated by these images, based on the strongly decreased deformation of the PA matrix. Distinct plastic deformations are observed in the near of the glass-fibers for pure PA 6. The fracture surface of the 50/50 composite looks similar to pure PA 6. In both cases, the glass-fibers display a good adhesion to the surrounding PA matrix. In contrast to this, the fracture surface of pure PA 66 shows less deformation of the matrix, and glass-fibers with less adhesion to the surrounding PA matrix. So it can be stated that the efficiency of the fibers decreases with increasing PA 66 content. This fact explains the decrease of the toughness with increasing PA 66 content.

As a main result of the investigations of the influence of mixing ratio can be summarized that the combination of PA 6 (good coloring) and PA 66 (small moisture absorption) was associated with a toughness deficit. The following results should clarify if this toughness deficit can become balanced by the addition of colorants.

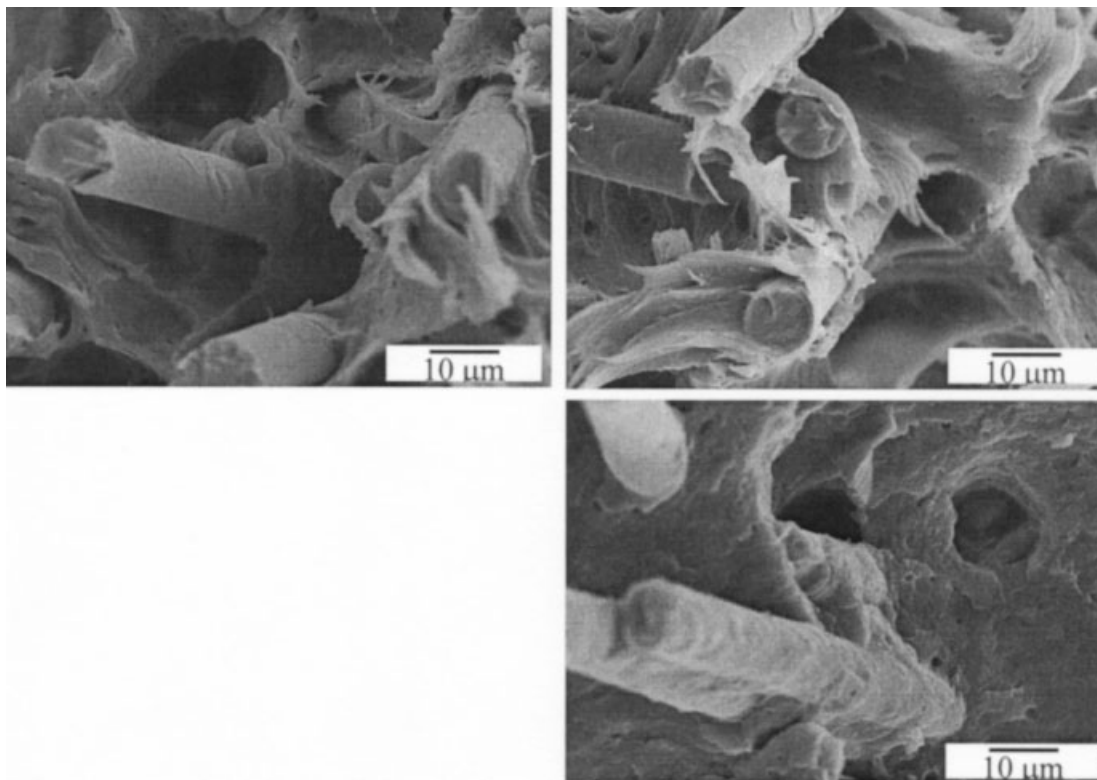


Figure 6 SEM images of fracture surfaces of pure PA 6 (top, left image), 50/50 composite (top, right image), and pure PA 66 (bottom), after stable crack growth.

Influence of the colorants

Basic characterization

A black-coloring of the PA composites proves as favorable, because of the priority application of these composites in the automotive industry. So, the influence of several black-colorants on mechanical and fracture mechanical properties of the PA composites was investigated.

Table II shows the results of tensile test (tensile strength, σ_M), and ball indentation test (hardness, H). The tensile strength is less changed, using the colorant carbon black, in comparison to the uncolored reference. In contrast to this, spinel and iron oxide decrease the tensile strength remarkably by about 17%. The hardness generally increases using

several colorants. The highest increase of the hardness is addressed to the colorant carbon black. In many cases, high hardness is combined with high resistance against scratching. Most common applications of PA in the automotive industry require such a high resistance against scratching (of surfaces), which caused the preferred use of carbon black for coloring.

Toughness characterization

Figure 7 shows the load-deflection behavior of the uncolored reference, and black-colored PA composites, respectively, for 50/50 mixing ratio. Also in this case, an a/W -ratio of 0.2 leads to unstable, and an a/W -ratio of 0.45 leads to stable crack growth. So a selective analysis of the crack growth behavior was possible.

The influence of several colorants (carbon black, spinel, iron oxide) on the resistance against unstable crack growth J_{Id} is shown in Figure 8. The toughness is remarkably changed by about 30%, using black-colorants, in comparison to the uncolored reference. The toughness decrease is similar for each colorant. So it can be noticed that the toughness deficit resulting from the combination of PA 6 and PA 66 becomes stronger, by adding carbon black, concerning the resistance against *unstable* crack growth.

TABLE II
Basic Characterization: Some Mechanical and Thermal Properties of Black-Colored PA Composites and Uncolored Reference

PA 6/PA 66 (wt %)	Tensile test	Ball indentation test
	σ_M (MPa)	H (N/mm ²)
50/50 uncolored	180 ± 2	158 ± 6
50/50 + carbon black	175 ± 2	184 ± 2
50/50 + spinel	150 ± 1	172 ± 1
50/50 + iron oxide	155 ± 1	170 ± 2

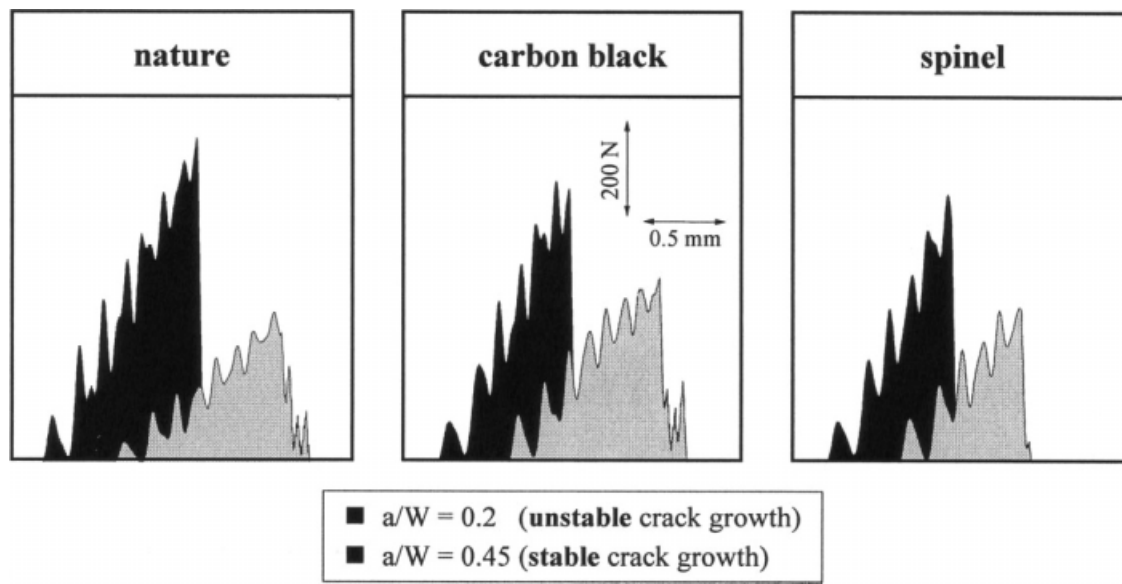


Figure 7 Load-deflection behavior of uncolored (left), carbon black-colored (center), and spinel-colored (right) PA 6/PA 66 (50/50).

To involve the evaluation of stable crack growth behavior in the toughness optimization of the PA composites, crack resistance curves were determined. Figure 9 is a plot of the tearing modulus T_J , i.e., the resistance against stable crack propagation as a function of the used colorants. Carbon black increases the tearing modulus by about 25% in comparison to the uncolored reference. In contrast to this, the colorants spinel and iron oxide decrease the

toughness significantly. Figure 10 shows SEM images of uncolored PA 6/PA 66 (left image) and carbon black-colored PA 6/PA 66 (right image), with 50/50 mixing ratio for both. The images illustrate the high toughness level of uncolored and carbon black-colored PA 6/PA 66. Distinct plastic deformations of the matrix, which can be observed, reveals high deformation energy, and consequently high toughness. The adhesion between PA matrix

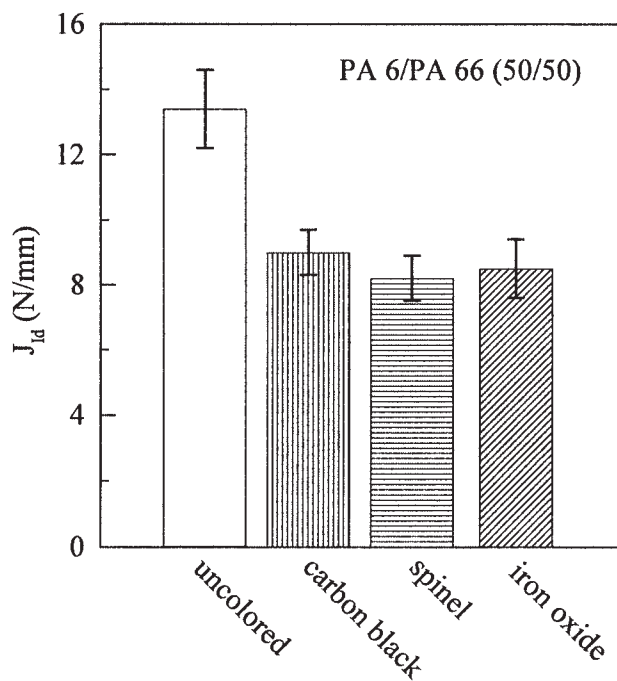


Figure 8 Influence of different colorants (carbon black, spinel, iron oxide) and of uncolored reference on resistance against unstable crack growth J_{id} .

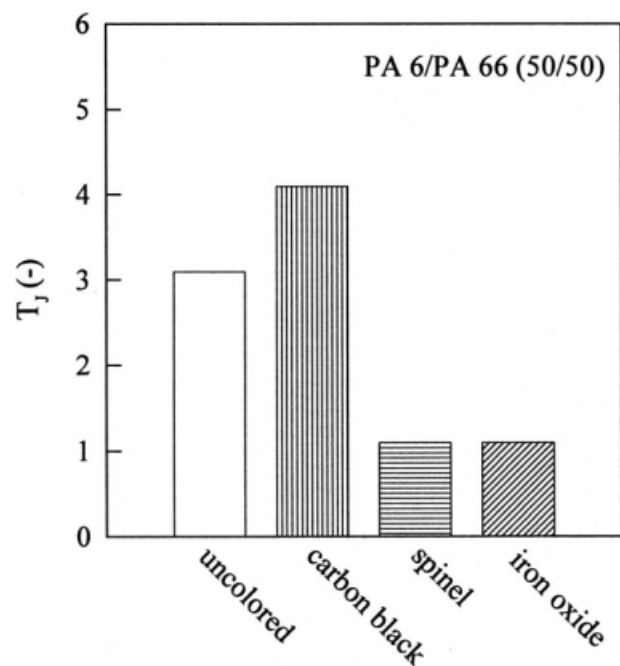


Figure 9 Influence of different colorants (carbon black, spinel, iron oxide) and of uncolored reference on resistance against stable crack initiation and propagation T_J (tearing modulus).

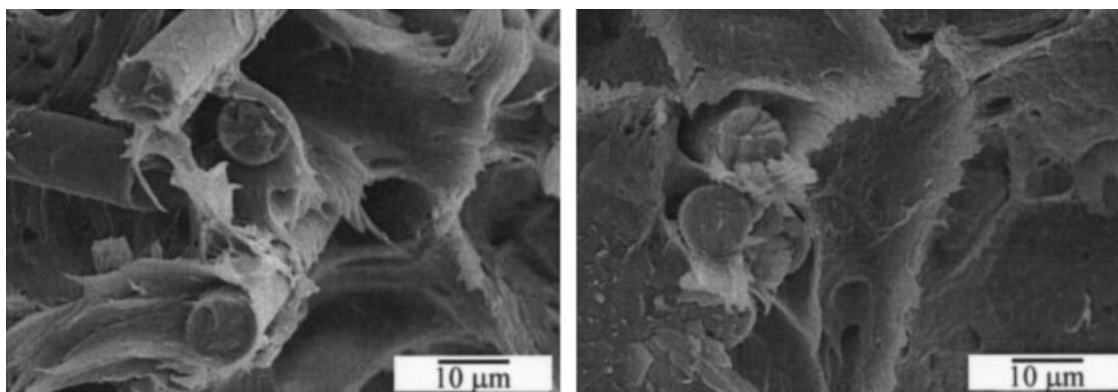


Figure 10 SEM images of fracture surfaces of uncolored and carbon black-colored PA 6/PA 66 (50/50) after stable crack growth.

and glass-fibers seems to be stronger for carbon black-colored PA 6/PA 66. Therefore, it can be speculated that the toughness increase using carbon black can be explained among others by higher adhesion between matrix and fibers.

The toughness deficit, which results from the combination of PA 6 and PA 66, can become balanced by the addition of carbon black concerning resistance against *stable* crack growth. The toughness increase of carbon black-colored PA composites could be determined only with crack resistance curves.

CONCLUSIONS

PA 6/PA 66 based composites are a combination of the good coloring of PA 6 and the small moisture absorption of PA 66. However, this combination is associated with a hardness and toughness decrease in comparison to pure PA 6. Both the hardness and the toughness deficit (concerning the resistance against stable crack growth) can become balanced by the addition of carbon black as an important black-colorant of the automotive industry. Adding carbon black, the toughness as resistance against stable crack growth is improved, and this distinct toughness increase could be determined only with fracture mechanics crack resistance curves. Thus, a characterization of the toughness was meaningful using the crack resistance curve method. Furthermore, the new cut method which enables the record of crack

All investigated PA specimens were moisture-free. However, PA changes their properties/characteristics by water absorption. Therefore, the influence of water absorption on toughness properties of the present investigated materials is to be analyzed in future work.

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