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Preparation and properties of composites of Kevlar-Nomex copolymer and boehmite

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SUMMARY:
 A new organic-inorganic hybrid material was prepared by incorporating boehmite into a Kevlar-Nomex copolymer via a sol-gel process. Poly(phenylene-terephthal-amide) chains having aminophenyltrimethoxysilane end groups were prepared by reacting a mixture of m- and p-phenylenediamine with terephthaloyl chloride, fol-lowed by end-capping with aminophenyltrimethoxysilane. The hydrolysis of the alkoxy groups of an aluminium sec-butoxide solution in butanol was carried out in the polymer matrix, thus creating an inorganic network structure combined chemi-cally with the aramid chains. Hybrid materials containing different proportions of boehmite in aramid were thus produced and films were cast by solvent evaporation technique. These films with up to 15 wt.-% of boehmite were yellow and transpar-ent, whereas the films with 20 wt.-% or more contents of boehmite were opaque. Mechanical properties of these films were analyzed. The values of tensile strength, initial modulus, toughness and maximum strain at rupture were initially found to in-crease and then decrease with further addition of boehmite. The tensile modulus of the hybrid material was found to be in the range of 3.0–4.5 GPa at 25 °C. These ceramers were found to withstand maximum tensile stress of the order of 252 MPa, and the thermal decomposition temperature was around 450 °C. The storage modu-lus as measured using DMTA was in the range of 7.6–18.9 GPa. The tan δ peak which in general became broader with increasing boehmite content showed a shoulder for composites containing large amounts of boehmite. The position of the peaks shifted towards high temperature with the increase in the inorganic contents showing hindrance in motion with increasing boehmite contents.

ZUSAMMENFASSUNG:
 Ein neuartiges organisch-anorganisches Hybridmaterial wurde durch den Einbau des Minerals Böhmit mittels eines Sol-Gel-Prozesses in ein Kevlar-Nomex-Copoly-meres hergestellt. Durch Reaktion eines Gemisches aus m- und p-Phenylendiamin mit Terephthaloylchlorid und anschließender Umsetzung mit Aminophenyltri-methoxysilan wurden Poly(phenylenterephthalamid)-Ketten mit Aminophenyltri-

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methoxysilan-Endgruppen synthetisiert. In dieser Polymermatrix wurde die Hydro-
lyse der Alkoxygruppen einer Lösung von Aluminium-sec-butanolat in Butanol
durchgeführt. Dadurch wurde ein chemisch an die Aramid-Ketten gebundenes anor-
ganisches Netzwerk aufgebaut. Aus den hergestellten Hybridmaterialien mit un-
terschiedlichen Böhmit-Gehalten in der Aramidmatrix wurden Filme gegossen. Die
Filme aus Hybridmaterial mit bis zu 15 Gew.-% Böhmit waren transparent gelb,
während bei 20 und mehr Gew.-% Böhmit opake Filme erhalten wurden. Die
mechanischen Eigenschaften dieser Filme wurden untersucht. Zugfestigkeit, Zug-
modul, Härte und maximale Bruchdehnung nahmen mit steigendem Böhmitgehalt
zunächst zu, verringerten sich jedoch bei weiterer Erhöhung des Mineralanteils wie-
der. Der Zugmodul des Hybridmaterials bei 25 °C lag zwischen 3,0 und 4,5 GPa.
Die Materialien hielten einer maximalen Zugspannung von 252 MPa stand und zeig-
ten Zersetzungstemperaturen von etwa 450 °C. Die mit DMTA ermittelten Werte für
den Speichermodul lagen im Bereich 7,6 – 18,9 GPa. Das tan δ-Signal verbreiterte
sich mit zunehmendem Böhmitanteil und ging bei hohen Böhmitgehalten in eine
Schulter über. Die Signalpositionen des Verlustfaktors wurden infolge der zuneh-
menden sterischen Einschränkung der Segmentbewegungen mit steigendem anorga-
nischen Anteil zu höheren Temperaturen verschoben.

Introduction

Different types of structural materials are used in order to meet the di-
verse requirements of industry. The most important among these are metals,
polymers and ceramics. Ceramics are useful due to their high thermal stabi-
lities, strength and high moduli, but their high density, high processing tem-
perature and very brittle nature discourage their use. Polymers on the other
hand, are much easier to process and are very tough, but are less thermally
stable. Among the polyamides, aramids have been particularly useful as
high-performance materials because of their very high thermal stabilities
and specific strength, their high degree of stiffness, and their low densi-
ties[1-3]. For example, the fibers produced from Nomex® and Kevlar® offer
outstanding tensile stength coupled with excellent high-temperature proper-
ties. They are competitive with steel and glass fibers in many applications,
in particular in the aerospace industry, where their relatively low densities
give them considerable advantages and thermal stability. The properties of
this class of polymers can be improved by incorporating a ceramic phase
such as silica[4-6], titania[7], boehmite[8] and zirconia[9]. In the last decade, the
idea of synthesizing organic-inorganic hybrid materials through the syner-
gistic combination of polymer and ceramic[10] to get intermediate properties
has gained popularity. One of the most important chemical routes to prepare
such composites is the sol-gel process[11-16]. In this way, one can readily pro-

duce novel organic-inorganic hybrid composites, frequently called "ceramers".

High-temperature polymers such as the aramids[1-3] are very difficult to treat in the usual sol-gel technique, but some studies have been carried out on a few aromatic polyamides[17-22], a number of polyimides[23-37], and several benzoxazole and benzobisthiazole polymers[38-44]. Ahmad and Co-workers[20,45,46] have prepared and analyzed two types of aramid-silica composite materials. In one type of aramid-silica hybrid materials, the polymer chains were not chemically linked to the silica, and, in the second type, the chains were chemically bonded to the silica network produced in-situ in the polymer matrix. The mechanical properties of the chemically bonded ceramers were compared with the corresponding system having an unbonded structure. It was observed that there was excellent improvement in the mechanical properties of the ceramers in which the organic and inorganic phases were chemically bonded as compared to non-bonded hybrid materials. Chemically linked zirconia-aramid ceramers containing up to 20% zirconia have also been reported by Rehman[9]. Thin films of pure aramid and hybrid ceramers were transparent and yellow in color. The increase in the tensile strength, toughness, initial modulus, and maximum stress at break has been observed with increase in the zirconia contents up to 10%, but then it decreased with further addition of zirconia. Chemically bonded titania-aramid composites have also been prepared by Sarwar[16]. Thin films of pure aramid and those of composites containing up to 20% titania in aramid were transparent. Maximum stress at break, initial modulus and toughness showed a large improvement up to 10% titania contents. However, the mechanical properties deteriorated beyond 15% titania in aramid. Boehmite-reinforced hybrid materials using poly(tetramethylene oxide) matrices have also been reported by Wilkes and Glaser[48].

In the present study, novel composite materials have been synthesized using boehmite as reinforcing phase in a copolymer of Kevlar-Nomex. The poly(phenylene terephthalamide) has been prepared by reacting a mixture of m- and p-phenylenediamine with terephthaloyl chloride in dimethyl acetamide. The copolymer chains endcapped with carbonyl chloride groups were then reacted with aminophenyltrimethoxysilane. The boehmite network was developed in-situ by mixing and hydrolyzing aluminium sec-butoxide in this copolymer solution. Thermal and mechanical properties of the composite films containing different percentages of boehmite have been studied.

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Experimental

The monomers used for the synthesis of aramid, 1,4-phenylenediamine, 1,3-phe-nylene-diamine and terephthaloyl chloride (TPC) were analytical grade reagents (Fluka) and were used as such. The anhydrous dimethyl acetamide (DMAC, 99%, Aldrich), aminophenyltrimethoxysilane (APTMOS, 97%), and aluminium sec-but-oxide (ASBO), both from Hüls America Inc.) were used as received.
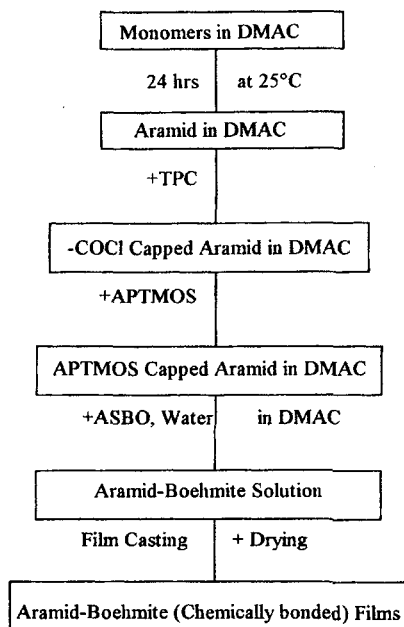
Preparation of aramid

The reaction was carried out in a 250 mL conical flask provided with a stirrer. A mixture of 1,4- and 1,3-phenylenediamine (50 mmol in 35:65 ratio) was taken and 150 g of the solvent DMAC was added to the flask. After complete mixing the amine solution was cooled to 0 °C. TPC (50 mmol) was added under complete anhy-drous conditions and stirring was continued at low temperature for 1 h. The tempera-ture of the flask was then raised to 25 °C. The reaction between diamines and diacid chloride is extremely fast and no change in viscosity is observed[49] after 30 min of reaction at 25 °C. This reaction, therefore, was assumed to be complete after 24 h. TPC (0.5 mmol in excess) was then added so as to endcap the chains with carbonyl chloride groups. To this reaction mixture, a stoichiometric amount of APTMOS was added to react with the carbonyl groups. Stirring was continued for additional 12 h at room temperature.

The polymer solution thus prepared served as a stock solution. Various propor-tions of ASBO were added to the polyamide solution, and after complete mixing a measured amount of water in DMAC was added to carry out the hydrolysis and con-densation of the inorganic network in each sample. Stirring of the reaction mixture was continued for further 6 h at 60 °C. The films from the samples containing var-ious amounts of boehmite were cast by baking out the solvent in an oven at 75–80 °C. Films thus formed were soaked in water to leach out any HCl produced dur-ing polymerization. These films were then dried at 80 °C under vacuum for 48 h. The preparation of the composite films is shown in Scheme 1. The reactions involv-ing hydrolysis and condensation of the boehmite network leading to the develop-ment of chemically linked ceramers are given in Scheme 2.

Mechanical properties of the hybrid material were measured at room temperature using an Instron Universal Testing Instrument TM-SM 1102 with a strain rate of 0.5 cm min^{-1}. Optical properties were recorded in the visible range at three different wavelengths (490, 530 and 600 nm) with a Shimadzu UV-Visible spectrophotometer. Dynamic mechanical thermal analysis was carried out in the temperature range 100–500 °C at a frequency of 5 Hz with a Rheometric Scientific DMTA III instru-ment. Thermogravimetric analysis was performed using a Netzsch Simultaneous Thermal Analyzer STA 429 in static air at a heating rate of 10 °C min^{-1}.

Scheme 1. Preparation method of aramid-boehmite films.

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          ┌──────────────────────────┐
          │    Monomers in DMAC      │
          └──────────────────────────┘
            24 hrs  │  at 25°C
          ┌──────────────────────────┐
          │     Aramid in DMAC       │
          └──────────────────────────┘
              +TPC  │
      ┌──────────────────────────────┐
      │  -COCl Capped Aramid in DMAC │
      └──────────────────────────────┘
           +APTMOS  │
   ┌─────────────────────────────────┐
   │  APTMOS Capped Aramid in DMAC   │
   └─────────────────────────────────┘
       +ASBO, Water │  in DMAC
     ┌───────────────────────────────┐
     │   Aramid-Boehmite Solution    │
     └───────────────────────────────┘
       Film Casting │  + Drying
 ┌────────────────────────────────────────┐
 │ Aramid-Boehmite (Chemically bonded) Films│
 └────────────────────────────────────────┘
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Soaking in water.
Drying under vacuum for 48 hrs.

Results and discussion

Thin films cast from composites of Kevlar-Nomex copolymer and boehmite (up to 15 wt.-%) were found to be transparent and yellow in color. The transmittance of the pure copolymer film with 0.15 mm thickness was 76.1, 76.5 and 83.4% at 490, 530 and 600 nm, respectively, being gradually reduced with increasing boehmite content. The films containing 20 wt.-% or more boehmite content were, however, opaque. As the inorganic network structure becomes extensive, there is an increasing tendency towards particle size growth. These particles agglomerate[50], their distribution becomes irregular and non-homogeneous making the films less transparent at higher boehmite contents.

Stress-strain curves of the pure copolymer and of the composites with various proportions of boehmite are shown in Fig. 1. The average values of the engineering stress obtained after 5 experimental tests have been quoted. It is
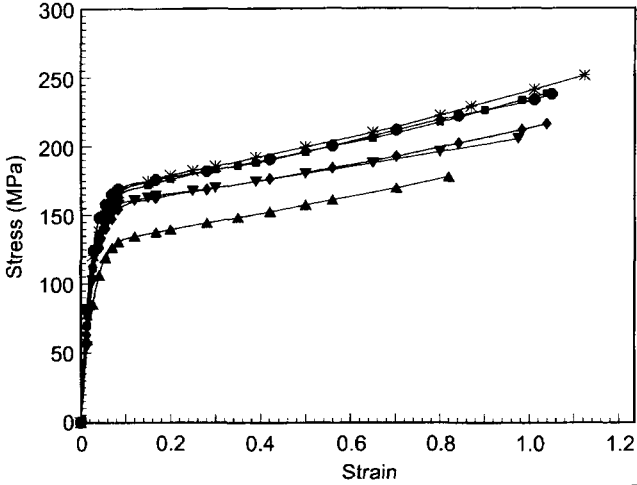
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Scheme 2. Hydrolysis and condensation of metal alkoxide to form metal oxide net-
work (a), structure of chemically linked ceramers (b).

(a) **Hydrolysis:**

$$M(OR)_3 + H_2O \longrightarrow (RO)_2M - OH + ROH$$

(R = Sec. Butyl)

Condensation:

$$\text{>}M - OH + HO - M\text{<} \longrightarrow \text{>}M - O - M\text{<} + H_2O$$

and / or

$$\text{>}M - OH + RO - M\text{<} \longrightarrow \text{>}M - O - M\text{<} + ROH$$

Net Reaction:

$$M(OR)_3 \text{ (Liq.)} \xrightarrow[\text{Cosolvent}]{H_2O / H^+ \text{ or } OH^-}$$

(b)

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Fig. 1. Tensile strength of aramid-boehmite composites with different contents of boehmite; (▲) 0 wt.-%, (■) 2.5 wt.-%, (*) 7.5 wt.-%, (●) 10 wt.-%, (♦) 15 wt.-%, (▼) 20 wt.-%.
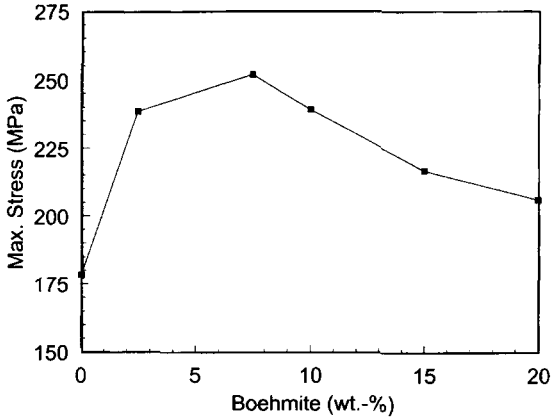
Fig. 2. Maximum stress at break vs. boehmite content of aramid-boehmite composites.

obvious from the figure that there is a significant increase in the tensile strength of the composite materials containing boehmite as compared to the pure aramid. The maximum stress at the break point increases initially and reaches its maximum (252 MPa) at 7.5 wt.-% boehmite content, showing

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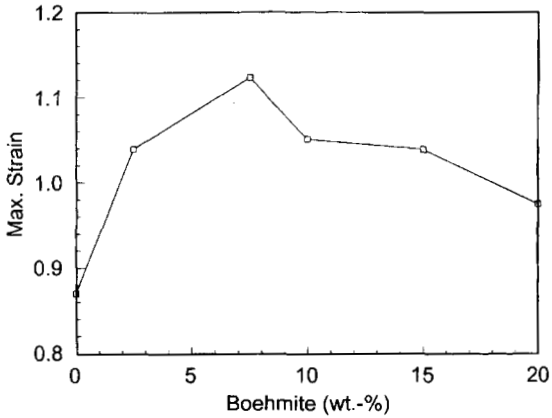
Fig. 3. Maximum strain at break vs. boehmite content of aramid-boehmite composites.

excellent improvement in the tensile strength. However, with further addition of boehmite this value decreased (Fig. 2). Films beyond 20 wt.-% boehmite were brittle and thus were not characterized for their mechanical behavior. The length at break also shows similar behavior (Fig. 3). The initial modulus calculated from the initial slopes of the stress-strain curves of pure polymer was 3.02 GPa and showed an increase with boehmite contents up to 10 wt.-% (4.43 GPa), but beyond this a decrease in the values of the modulus was observed (Fig. 4).
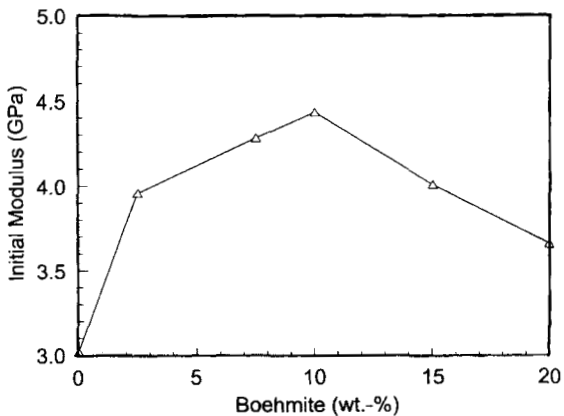
Fig. 4. Initial modulus vs. boehmite content of aramid-boehmite composites.
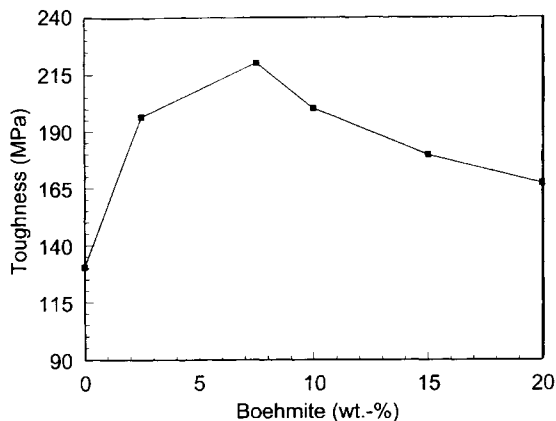
Fig. 5. Toughness vs. boehmite content of aramid-boehmite composites.

The toughness of these composites was measured by calculating the area under stress-strain curves. Fig. 5 shows the toughness of pure aramid and boehmite composite materials. It indicates that the toughness of the material undergoes first an increase up to 7.5 wt.-% boehmite content, but then a sharp decrease is observed with higher boehmite contents. End-linking of the copolymer chains with the boehmite network provides a large amount of reinforcement to hybrid materials. However, for a given molecular weight of the polymer, there is a particular number of end-groups which can be linked to the inorganic phase. If the boehmite content is increased beyond 7.5 wt.-% it seems that the excess boehmite particles may not be linked with copolymer chains so the mechanical properties of the composites deteriorate after further addition of the inorganic component.

DMTA was also carried out on the samples containing various proportions of boehmite in aramid. The temperature variation of the storage modulus (bending) is shown in Fig. 6. The storage modulus initially increases with an increase in the boehmite content, and then slightly decreases. The inorganic network has less free volume and is less flexible as compared to the organic phase. Increased proportions of this network increase the storage modulus. However, when the amount of inorganic network increases beyond a certain limit, the inorganic structure tends to agglomerate to small particles. This porous structure has less cohesion with the organic matrix which result in a low modulus. At higher temperatures a sharp decrease in modulus was oberved due to the onset of the thermal motion. Fig. 7 shows the variation of the loss tan δ vs. temperature of the composites containing various
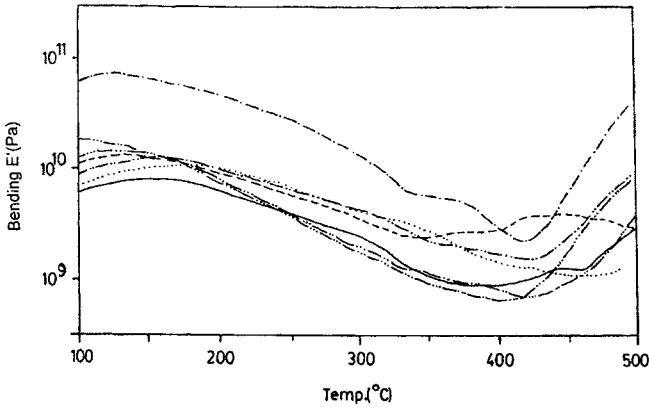
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Fig. 6. Temperature dependence of the storage modulus of aramid-boehmite composites at 5 Hz; boehmite content: (—) 0 wt.-%, (···) 2.5 wt.-%, (- - -) 5 wt.-%, (-·-) 7.5 wt.-%, (-···-) 10 wt.-%, (-····-) 15 wt.-%, (-····-··) 20 wt.-%.
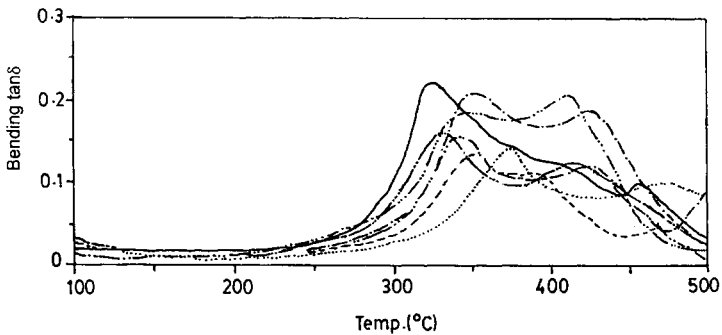

Fig. 7. Variation of the loss tangent tan δ with temperature of aramid-boehmite composites at 5 Hz; boehmite content: (—) 0 wt.-%, (···) 2.5 wt.-%, (- - -) 5 wt.-%, (-··-) 7.5 wt.-%, (-···-···-) 10 wt.-%, (-····-····-) 15 wt.-%, (-····-···-) 20 wt.-%.

proportions of boehmite. It is apparent from the figure that with an increase in temperature, a stage is reached when the onset of the segmental motion starts. At this temperature a sharp increase in tan δ is observed. In case of pure aramid a sharp peak is observed at 325 °C. In case of hybrid materials the peak splits up into two portions, showing a maximum around 350 °C and a shoulder at higher temperature. The first maximum corresponds to the pure copolymer chains while the second maximum corresponds to the poly-

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mer chains linked with the inorganic network. The introduction of the inorganic network reduces the segmental motion of the polymer chains, and as the proportion of the inorganic network increases the position of the second maximum shifts towards higher temperature. The intensity of the peaks decreases and becomes broader in general with increased boehmite content.

Thermal properties of pure aramid and aramid-boehmite composites were studied in static air at a heating rate of $10\,^\circ$C min^{-1}. Fig. 8 indicates that the
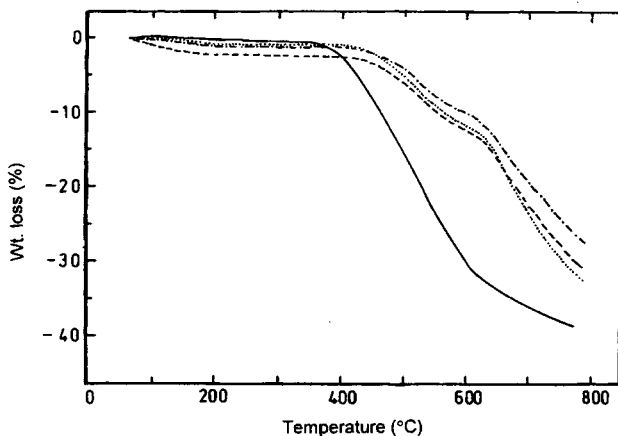
Fig. 8. TGA curves of aramid-boehmite composites with different contents of boehmite; (—) 0 wt.-%, (···) 2.5 wt.-%, (- - -) 5 wt.-%, (-·-··-) 15 wt.-%.

thermal decomposition temperature of all the samples is in the range of $400-450\,^\circ$C. The initial weight loss around $100-150\,^\circ$C may be due to partial dehydration of γ-AlO(OH). At higher temperature some phase changes may occur yielding γ-Al$_2$O$_3$. As the boehmite content in the composites increases, the weight retained at $800\,^\circ$C also increases. In general, the composite materials show good thermal stability up to $450\,^\circ$C.

Conclusions

Aramid-boehmite composites have been prepared via a sol-gel process. These composites are transparent and yellow in color. The chemical bonding between the inorganic and organic phases provides significant enhancement in the mechanical strength over the pure copolymer. However, only an appropriate proportion of the two phases provides greater cohesion and thus

an optimum tensile strength is observed which in this case is at 7.5 wt.-% boehmite content in the copolymer matrix. These composites are thermally stable up to 450°C and can be very useful as matrix for advanced applications.

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