SILICA NANOPARTICLES & RUBBER TOUGHENING – A SYNERGY IN ADHESIVES & COMPOSITES

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TOPICS

- Rubber-toughened thermosets
- Surface-modified silica nanoparticles
- RLP and nanoparticles: the synergy in epoxies
- Adhesives & composites performance
- Summary & Outlook
RUBBER-TOUGHENING OF THERMOSETS

- Well-known technology used in most structural epoxy adhesives, many prepreg and filament winding applications, some injection applications (e.g. VARTM)

- Used for epoxies, vinyl esters, unsaturated polyester resins

- Improved properties:
  - increased toughness, reduced brittleness
  - improved mechanical properties

- Some drawbacks:
  - higher resin viscosity
  - lower Tg, modulus
RUBBER-TOUGHENING OF THERMOSETS: MECHANISM

Kinloch et al., J. Mat. Sci 27, 2763-2769 (1992)
"CLASSIC" FUMED SILICA – SILICA NANOPARTICLE

agglomerates, branched structures, thixotropic properties

isolated particle (from Odegard et al. Polymer 46 (2005), 553
THE nanoresins AG PROCESS

Aqueous Sodium Silicate Solution

Silica Sol

Surface modification

Matrix exchange

Agglomeration, gelation, flocculation

particle concentrate

Low viscous, waterclear, no sedimentation
PARTICLE SIZE AND DISTRIBUTION (TEM, SANS)

isolated, spherical, uniform particles
VISCOSITY $\eta$ AS FUNCTION OF SiO$_2$ CONTENT

(cycloaliphatic bisepoxide EEC; $T = 25^\circ$C)

low viscous, transparent products
NANO-TOUGHENING OF EPOXIES: MECHANISM I

(a) Crack tip

(b) Fracture surface

Data courtesy of IVW
NANO-TOUGHENING OF EPOXIES: MECHANISM I

high deflection of crack growth with nanoparticles

data courtesy of IVW
NANO-TOUGHENING OF EPOXIES: MECHANISM II

glass microspheres in epoxy resins toughen:

debonding and plastic void formation on the fracture surface

similar mechanism with SiO$_2$-nanoparticles!

Kinloch et al, J. Mat. Sci. 20, 4169, 1985
NANO-TOUGHENING OF EPOXIES: FATIGUE

DGEBA, anhydride cure

dramatically improved fatigue properties by the addition of SiO$_2$-nanoparticles
RUBBER TOUGHENING + SILICA NANOPARTICLES: THE SYNERGY

- **silica nanoparticles** increase modulus, stiffness, compression strength, bending strength, fatigue properties and toughness

- **silica nanoparticles** cannot replace rubber toughening

- **combining** combining rubber toughening with silica nanoparticles tough and stiff systems can be formulated

- a **synergy** exists and toughness is increased further
RUBBER-TOUGHENED EPOXY WITH NANOPARTICLES

rubber domains (from CTBN adduct) & silica nanoparticles

picture courtesy of Army Research Lab
HEAT CURING EPOXY ADHESIVES

1 part paste adhesive
77.5 parts DGEBA/
    Nanopox®
37.5 parts CTBN adduct
2 parts fumed silica
4 parts Dicy
2 parts accelerator
ADHESIVES: LAP SHEAR STRENGTH (1 PART EPOXY)

untreated automotive aluminium, cured 30 min 180 °C
MODULUS

1 part epoxy, cured 30 min 180 °C

DIN ISO 178
AMBIENT TEMPERATURE CURING EPOXY ADHESIVES

A-part:
DGEBA/Nanopox®

B-part:
66 % Polypox® P 502
34 % ATBN
ADHESIVES: FRACTURE ENERGY (2 PART EPOXY)

untreated automotive aluminium, cured 24 h RT + 2 h 60 °C

G1c according to BS 7991
ADHESIVES: ROLLER PEEL, WEDGE IMPACT (2 PART EPOXY)

2024 T3 aluminium; automotive steel, cured 24 h RT + 2 h 60 °C
AMBIENT TEMPERATURE CURING EPOXY ADHESIVES

**A-part:**
DGEBA/DGEBF/
Nanopox®
3 parts fumed silica
(+CTBN-Adduct=23.7%)

**B-part:**
40 % ATBN 1300x16
30 % Polypox® P 502
20 % Jeffamine® D 400
10 % Isophoronediamine

Source: Vestas
2 part epoxy, supertough, very thixotropic, 24 h RT + 2 h 60 °C

DIN 55-283

% nanosilica

MPa

10 11 12 13 14 15 16 17 18 19 20

0 2 4 6 8 10 12

15.6 % RLP

23.7 % RLP
2 part epoxy, supertough, very thixotropic, 24 h RT + 2 h 60 °C
LAP SHEAR STRENGTH GFRC

2 part epoxy, supertough, very thixotropic, 24 h RT + 2 h 60 °C
COMPOSITES: CFRC TOUGHNESS

DGEBA, anhydride cure, 1 h 90 °C, 2 h 160 °C; VARTM
COMPOSITES: CFRC GIc VERSUS GIIc

DGEBA, anhydride cure, 1 h 90 °C, 2 h 160 °C; VARTM
COMPOSITES: FRC TOUGHNESS

summary of VARTM and RTM made laminates
COMPOSITES: CFRC FALLING DART TEST

TGMDA, aromatic amine cure, 2 h 180 °C, RTM

Control

30 J Impact

8 % CTBN, 10 % nanoparticles

data courtesy of EADS
SUMMARY

- combining "classic" Hypro™ RLP (former Hycar® RLP) toughening with Nanopox® nanoparticles adhesives and composites with superior properties can be manufactured (tough and stiff!)

- epoxy adhesives using the synergy between rubber toughening and silica nanoparticles are commercially available (automotive, aerospace, electronics,...)

- composite parts for automotive, machine construction, sports equipment etc. are significantly improved using the synergy (such products are in the market since years)
OUTLOOK: MAJOR CURRENT R&D ACTIVITIES

- detailed investigation in the mechanisms of the synergy
- vinyl ester resins with nanoparticles and rubber
- 2 part epoxy adhesives for wind mill blade bonding
- UV cured acrylic adhesives for automotive
- glass fiber reinforced composites made with nanosilica and RLP modified vinyl ester resins