

VISCOELASTIC MODELLING OF STRESS-STRAIN-BEHAVIOR OF TWO PHASE MODEL MATERIALS (ABS AND PCL-TPS (POLY-ε-CAPROLACTONE / THERMOPLASTIC STARCH) BLENDS)

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Objectives:

The scope of this study was to predict macroscopic mechanical composite properties based on a new “atomistic” microscale materials model called Elementary Volume Concept (EVC). Models by Halpin-Tsai¹ or Tandon-Weng² are state of the art in materials modelling using continuum approaches to describe effects of dispersed short fibres or fillers on Young's moduli only.

Introduction:

The stress-strain-behavior of homo-polymers and statistical copolymers can be well described by a viscoelastic stress-strain-function (VSSF) based on the MAXWELL-Model [3]

$$\sigma(\varepsilon) = E \varepsilon_R \frac{(1 - e^{-\frac{\varepsilon}{\varepsilon_R}})}{1 + 2\mu\varepsilon} \cong E \varepsilon_R (1 - e^{-\frac{\varepsilon}{\varepsilon_R}}) \quad (1)$$

$\varepsilon < \varepsilon_R$

with stress σ , strain ε , Young's modulus E , relaxation strain ε_R and Poisson ratio μ . For polymers containing a disperse phase (2nd polymer, glass spheres, filler particles etc.) it would be interesting to use Eq.(1) to describe the stress-strain-behavior of both matrix and disperse phase, and to introduce effects of the volume content of disperse phase v_F via a phase model. This model attributes for the load transfer between matrix and disperse phase to calculate the mechanical behavior of polymers having any volume content v_F .

Materials and Methods:

Test bars of type 1B were manufactured of

- Acrylonitrile butadiene styrene (ABS) model materials with defined butadiene contents ($w_F = 7.5\%, 15\%, 22.5\%, 30\%$) having particle sizes of 100 nm and 400 nm in various fractions, and
- PCL, TPS, and PCL-TPS-blends having mass fraction ratios of 60/40, 50/50, 40/60, 30/70 and 20/80. The TPS component was softened using 25% glycerol.

Volume fractions were calculated using the mass fractions by means of density measurements of each mixture ratio.

Tensile tests were performed according to ISO 527 using a ZWICK 1476 tensile testing machine with a strain rate of 10%/min.

Young's moduli E and relaxation strains ε_R were determined by curve fitting of stress-strain-curves using the VSSF (Eq. 1).

Modelling with the EVC:

The Elementary Volume Concept (EVC) assumes that the mechanical behavior of any material is represented by the behavior of an elementary volume (EV) containing a single inclusion, Fig. 1 (left). In order to determine the mechanical behavior of the EV, it is divided in a matrix part and composite part in series, Fig. 1 (right). It is obvious that the strains of EV ε_{EV} , matrix part ε_M and composite part ε_F differ but are related to each other

$$\varepsilon_{EV} = \frac{1 + d - k}{1 + d} \varepsilon_M + \frac{k}{1 + d} \varepsilon_F \quad (2)$$

with normalized inclusion distance $d = \frac{a}{D}$ and efficiency faktor k taking into account the inclusion geometry.

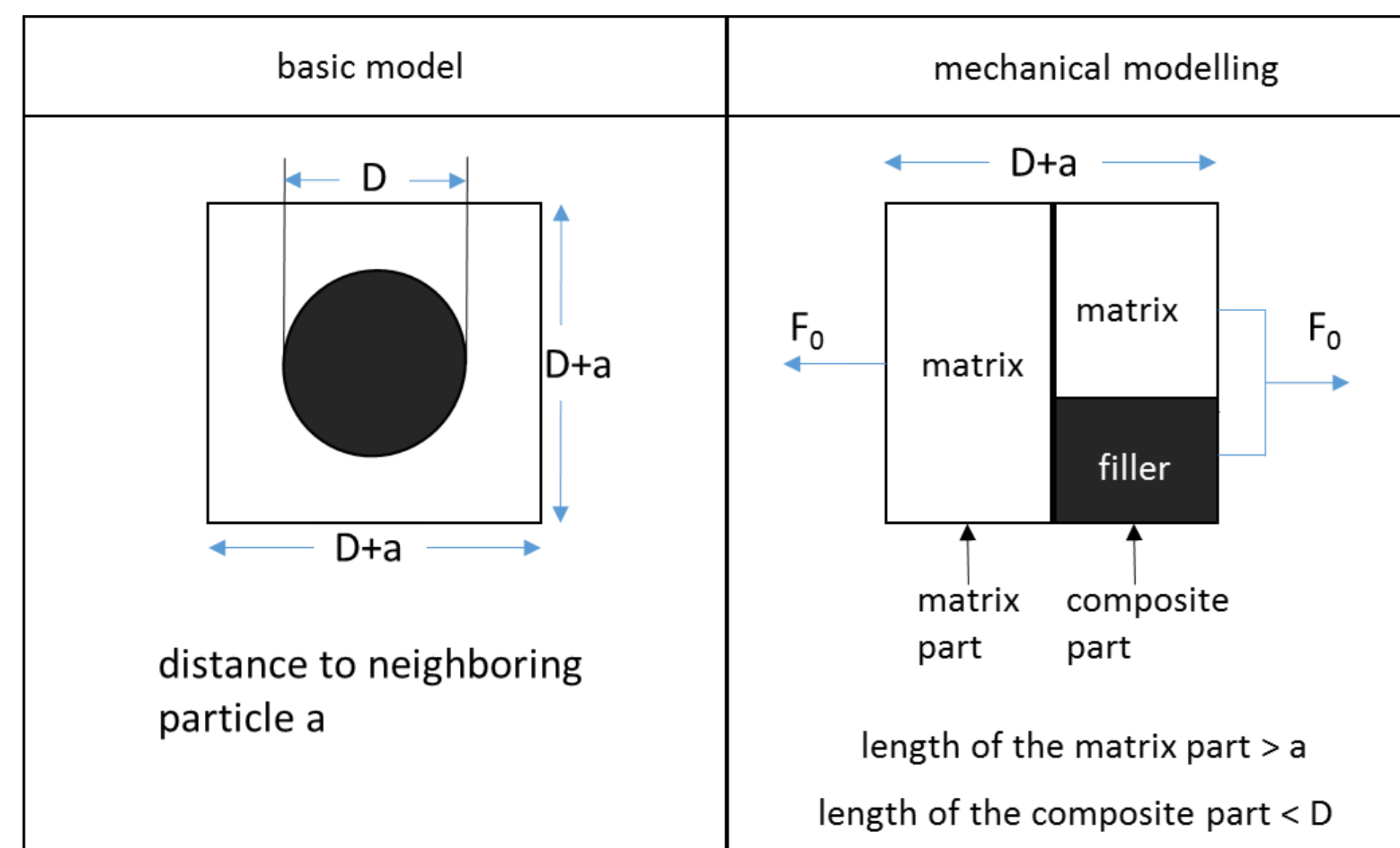


Fig.1: EV of matrix with “dispersed” spheres or filler (left) and its division in matrix part and composite part (right)

In case of two different disperse phases one obtains a filler volume fraction dependent relation for the Young's modulus.

$$E = x_{100nm} E_M \frac{1 + v_F^{2/3} \frac{E_F^{100nm} - E_M}{E_M}}{1 + v_F^{2/3} (1 - v_F^{1/3}) \frac{E_F^{100nm} - E_M}{E_M}} + (1 - x_{100nm}) E_M \frac{1 + v_F^{2/3} \frac{E_F^{400nm} - E_M}{E_M}}{1 + v_F^{2/3} (1 - v_F^{1/3}) \frac{E_F^{400nm} - E_M}{E_M}} \quad (3)$$

with filler portion x_{100nm} for small particles, Young's moduli E where M and F denotes matrix and filler. Eq.3 holds for the ABS model materials containing two different particle sizes. If there is only one kind of disperse phase the second term of Eq.3 vanishes and only the black term remains. As $v_F = \frac{k^3}{(1+d)^3}$ one can introduce effects of matrix-filler-adhesion by multiplying k with an adhesion factor k_{adh} .

Results and discussion:

The Young's moduli of ABS depend highly on the butadiene content as well as the particle size distribution of small and large particles. With increasing butadiene content and larger particle fraction the modulus decreases. Modelling this behavior with the EVC the calculated values (blue and green bars) fit the progression of the measured values, but only the calculated values considering the adhesion factor $k_{adh}=1.18$ (green bars) are in good agreement with the measured values within the standard deviation, Fig.2.

Young's moduli of PCL-TPS blends decrease with increasing TPS content. The blends show that a phase inversion occurs if the TPS content exceeds 70%. Therefore Young's moduli are calculated for the two cases: PCL and TPS as matrix materials separately, Fig. 3.

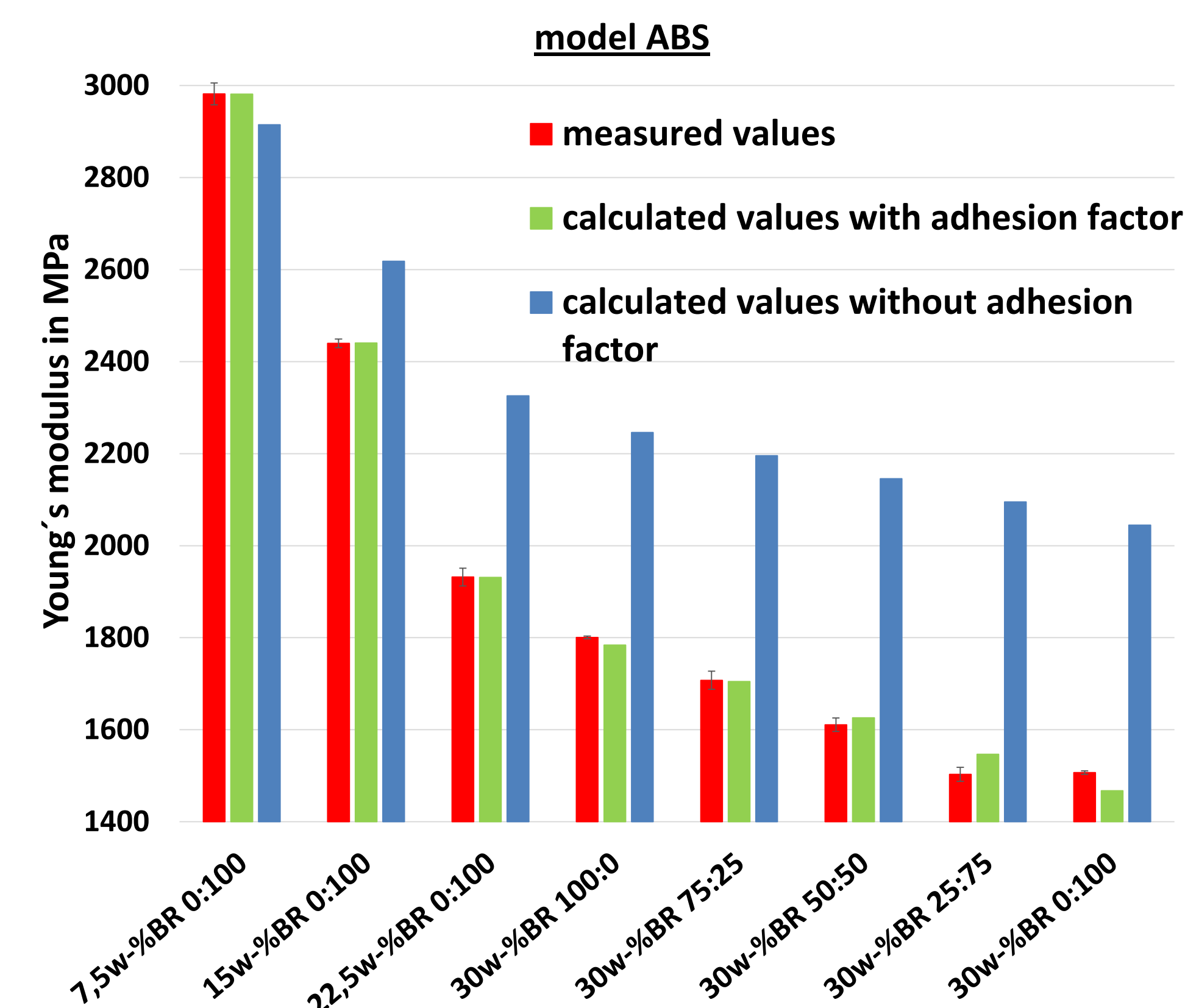


Fig.2: Calculated Young's moduli of ABS model materials due to Eq.3 compared to measured ones.

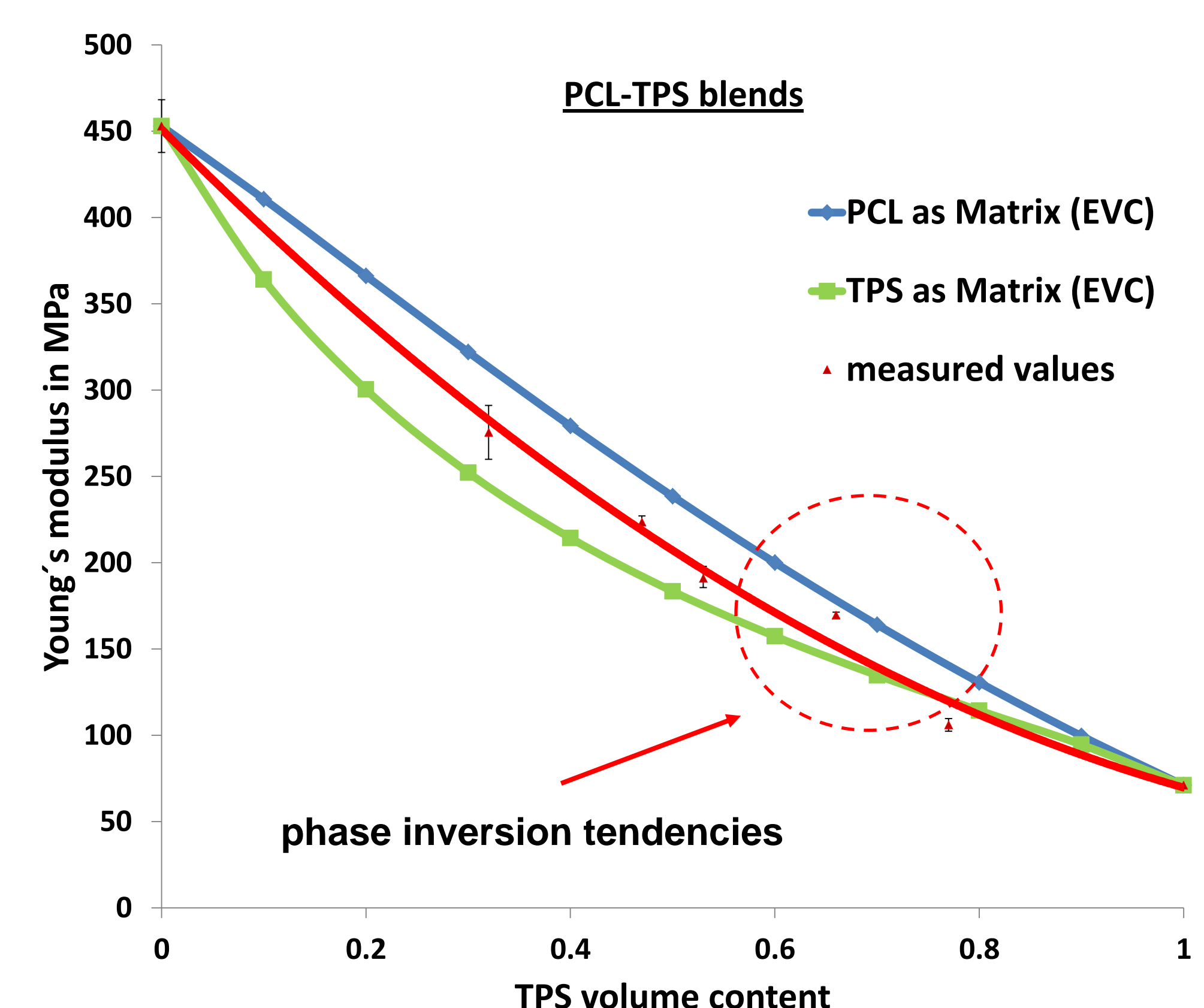


Fig.3: Calculated Young's moduli of PCL-TPS blends due to Eq.3 compared to measured ones.

Conclusions:

It is shown that regardless of the phase character of the composites the EVC is able to predict well the measured stiffnesses within the standard deviations. Effects of filler geometry can be taken into account as well as adhesion or reinforcing effects of the interface. Furthermore, it allows for calculating the stiffness of any mixture ratio of matrix and disperse phase.

The modelling of ABS and the dependency of its mechanical properties on butadiene content as well as particle size shows that the interface properties differ from matrix and particle.

The modelling of the PCL-TPS blends shows that the description phase inversion effects with changing composition ratios becomes possible.

References:

- [1] J. C. Halpin, J. L. Kardos, The Halpin-Tsai Equations: A Review, 1976
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