THE INFLUENCE OF THERMOPLASTIC ELASTOMERS ON MORPHOLOGICAL AND MECHANICAL PROPERTIES OF PP/TALC COMPOSITES[†]

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Abstract: Recent investigations have shown that modification of polymer matrix with filler and elastomers significantly affects composite's mechanical properties. Isotactic PP modified with either untreated or treated talc and either SEBS or SEBS-gMA were used in these investigations. Samples were prepared by melt-mixing in a Brabender kneading chamber and were compression molded into plates on a laboratory press. The composites were characterised by measuring mechanical properties (Young's modulus, yield stress, notched impact strength) and by defining morphology. Binary sistems PP/talc and PP/elastomer containing up to 16 vol.% of talc and up to 10 vol.% of elastomer, as well as ternary PP/talc/elastomer composites with 12 vol.% talc were investigated. Ternary composite's yield stress was also calculated b semiempirical equations. We have found out, that the use of treated modifiers (talc or elastomer) improves adhesion with matrix, which reflects on mechanical properties as better stress transfer.

Introduction

An important recent development in polymeric materials concerns the preparation of hybrid particulate composites obtained by incorporating both rubbery and inorganic particles into a polymer matrix.

The addition of the elastomeric phase enhances the material toughness, whereas the addition of inorganic fillers increases the material stiffness. Combination of filler and elastomer compensate either elasticity or strength reduction which can rise by introducing in PP matrix only one component (either talc or elastomer). Moreover,

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[†]Dedicated to the memory of Professor Dr. Anton Šebenik

addition of both components can offer other advantages such as reduction in cost, a good surface appearance, and improved processing behaviour [1].

Among thermoplastics polypropylene (PP) is outstanding with respect to its attractive price/performance ratio combined with heat distortion temperature above 100ºC, and high stiffness.

Poor adhesion between filler and PP is a primary cause of low strength and poor thermomechanical properties, especialy at high filler volume fractions [2]. Therefore, PP is frequently toughned by incorporationg elastomer microparticles, e.g. by blending of PP with elastomers [3,4].

This paper describes the influence of thermoplastic elastomers (TPE-s) on morphology development and mechanical properties, e.g. stiffness, strength, and toughness of talc-reinforced PP. Two thermoplastic elastomers were used, block poly-(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) and the corresponding block copolymer grafted with maleic anhydride (SEBS-gMA). Pure or aminosilane-functionalized talc was blended together with PP in a Brabender kneader. Morphology and mechanical properties were studied as a function both type and volume fraction of TPE. The comparison of theoretical and measured values of mechanical properties is discused.

Experimental

Materials

For preparation of binary PP/talc and PP/ elastomer systems, as well as ternary PP/talc/elastomer composites, the folowing materials were used:

- polypropylene (PP) Novolen 1100 L (BASF), MFI=6g/10min, ρ=0.908g/cm^3, Mn=47000*, Mw/Mn=9.3*

- untreated talc, Talk Naintsch A-20 (Luzenac), particle size (top cut)= 20μm, ρ=2.8g/cm^3, specific surface = 24000 ^{2}/g

- talc with aminosilane surface treated (2%), Talk Naintsch A-20 V592 (Luzenac), particle size (top cut)= 20μm, ρ=2.8g/cm^3. specific surface = 24000 ^{2}/g

- block poly-(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) Kraton G-1650 (Shell), styrene/rubber ratio=28/72, ρ=0.91g/cm^3, Mn=92400*, Mw/Mn=1.19*

- block poly-(styrene-b-ethylene-co-butylene-b-styrene) grafted wit maleic anhydrid (SEBS-gMA) Kraton KG-1901 (Shell), styrene/rubber ratio=29/71, ρ=0.91g/cm^3, Mn=47300*, Mw/Mn=1.55*

(*/ Values were determined by size exclusion chromatography.)

Sample preparation

Binary PP/talc and PP/elastomer systems with talc ratio 4, 8, 12 and 16 vol.% and elastomer ratio 2.5, 5 and 10 vol.%, as well as ternary PP/untreated talc/elastomer and PP/treated talc/elastomer composites with 12 vol.% of talc and elastomer content of 2.5, 5 and 10 vol.% were prepared in a Brabender kneading chamber. Into a chamber a 200ºC and rotor speed 50 min^{-1} first the filler was added and after 30s PP with elastomer. After that, the samples were kneaded for 6 more minutes. The melt was pressed into 1 and 4 mm plates on laboratory press. The pressing temperature was 220ºC, pressure 100 bar, pressing time 14 min for 1mm and 9.5 min for 4 mm thick plates. Plates were cooled to room temperature in the air.

Test methods

Tensile properties (Young's modulus, yield stress) were measured by Zwick 147670 Z100/SN5A apparatus at 23°C and strain rate of 2mm/min (ISO 527).

Notched impact strength was measured according to Charpy test (DIN 53453) by Zwick apparatus at 25°C.

Scanning electron microscope (SEM) Jeol JSM 840-A was used to study the morphology, magnification was 2000- and 9000-times at acceleration voltage 10kV. Samples were fractured in liquid nitrogen and covered with gold before examination by the microscope.

Results and discussion

Young's modulus of PP hybrid composites containing both talc and elastomer, measured as slope of strain-stress curve, determined as a function o elastomer type and volume fraction (φ_e), is depicted in **Fig.1**. As expected, the hybrid composite moduli decreased with increasing elastomer volume fraction. Values of Young's moduli of PP

hybrid composites containing SEBS are higher than that of corresponding hybrid composites containing SEBS-gMA.
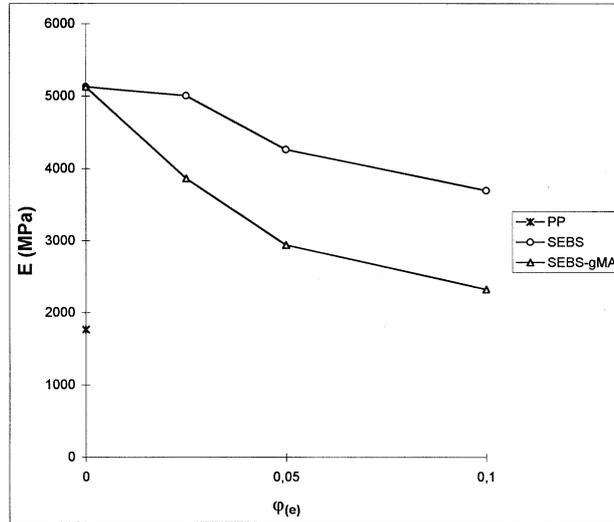
Figure 1: Young's modulus of pure PP and modified PP/treated talc composites as a function of elastomer volume fraction at talc content 12 vol.%

In previous work [5] it was shown that in PP/talc/SEBS systems SEBS is dispersed as separate phase, while at PP hybrid composite with treated talc, SEBS- gMA can encapsulate talc particles to form core-shell particles consisting of talc core and SEBS-gMA shell (**Fig.2**). The size of dispersed particles depends on SEBS molecular weight and on SEBS content.
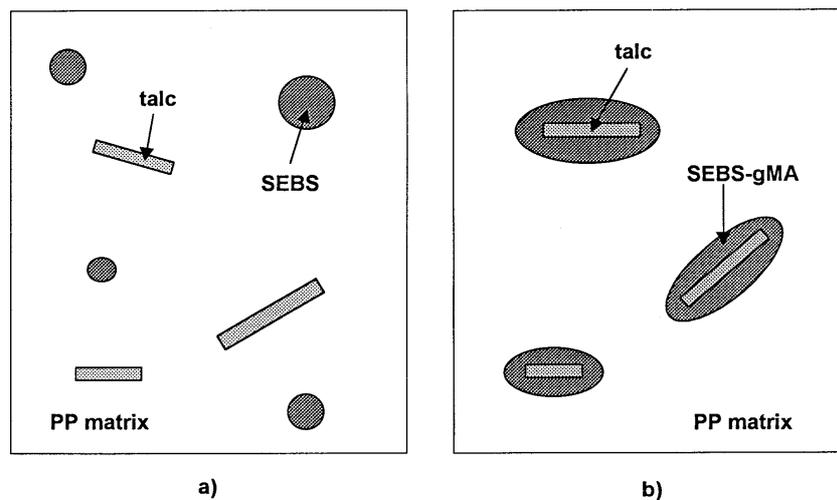
Figure 2: Morphologies of PP hybrid composites: a) three phase morphology with separately dispersed elastomer and filler particles b) two phase morphology with core-shell particles (filler particle core and elastomeric shell)

At binary PP/talc composites, talc particles significantly increase stiffness and at filler volume fraction 12 % practically don't affect the tensile strength at yield [6].

In ternary composites with SEBS-gMA, the addition of talc, as elastomer subinclusion, should decrease volume fraction of PP and contribute to form thin interlayer o elastomer. Matonis and Small [7] proposed that very thin elastomeric interlayers with thickness of about 1/1000 of particle diameter between filler and matrix increase Young's modulus, whereas thicker surface interlayers decrease modulus. From Fig.1 it is obvious that thicker interlayers of elastomeric shells are formed, which is related to molecular weights of used elastomers and size distribution of talc particles [8].

SEM studies of cryo-fractured surfaces of PP/treated talc/ elastomer composites are presented in **Figs.3 (a-e)**. SEM images of fractured surfaces of PP hybrid composites, containing 12 vol.% talc and 5 vol.% SEBS or SEBS-gMA, show sufficient adhesion between filler and matrix. SEBS is randomly dispersed in matrix, higher volume fraction is reflected as a strong coalescence. In case of using up to 5 vol.% SEBS-gMA, the elastomer particles are located on talc surface and the surface is very diffuse, owing to quality of interfacial adhesion. At 10 vol.% of SEBS- gMA first core-shell is observed, the talc surface is less diffuse and SEBS-gMA particles are present. From SEM images it is not clear wheather these particles are also core-shell formations or particles of pure SEBS-gMA.

Tensile yield stress, determined at large deformations, is an excellent measure for interfacial interactions in heterogeneous polymer systems [9,10]. With the help of the theory of tensile yield stress it is possible to determine a parameter related to stress transfer of blends and filled polymers. Pukanszky [11] derived an equation for blends and composites with one single dispersed phase:

$$\sigma_y = \sigma_{y0} \cdot \frac{1-\varphi_d}{1+2.5\varphi_d} \cdot \exp(B\varphi_d) \qquad (1)$$

where σ_y is the yield stress of the blend and composite, respectively, and σ_{y0} the matrix yield stress. φ_d is the volume fraction of the dispersed phase.
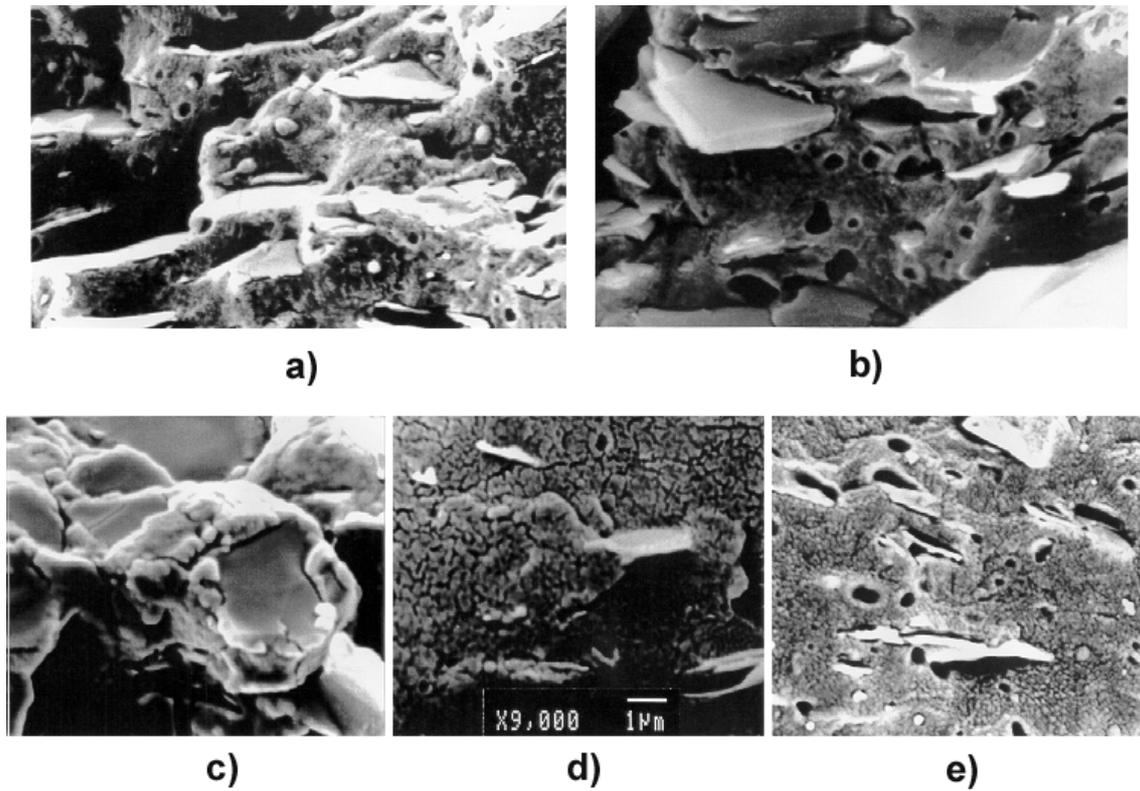
Figure 3: Scanning electron micrographs of hybrid composites; a) surface of unextracted PP with 12 vol.% treated talc and 5 vol.% SEBS, b) surface of xylene extracted PP with 12 vol.% treated talc and 5 vol.% SEBS, c) surface of unextracted PP with 12 vol.% treated talc and 5 vol.% SEBS-gMA, d) surface of xylene extracted PP with 12 vol.% treated talc and 5 vol.% SEBS-gMA, e) surface of xylene extracted PP with 12 vol.% treated talc and 10 vol.% SEBS-gMA

The second factor takes into account the smaller effective load-bearing cross section by replacing matrix polymer by dispersed phase. Parameter *B* in the third factor considers stress transfer between dispersed phase and matrix and indicates irregular structures or processes (aggregation, orientation of anisotropic filler particles), what can considerably influence the yield stress. Strong interfacial interactions lead to high values of *B* and consequently to high yield stress of corresponding system. Higher specific surface and anisotropy of filler is reflected in higher values of parameter *B*, while aglomeration and surface treatment of filler have an opposite effect.

Parameter *B* can be evaluated from experimental data in form o linearized graph. There are two possibilities of linearisation. The first one assumes a tensile yield stress o matrix (σ_{y0}) to be constant and equation can be linearized as follows:

$$\ln\left(\frac{\sigma_y}{\sigma_{y0}} \cdot \frac{1+2.5\varphi_d}{1-\varphi_d}\right) = \ln\sigma_{y(rel.)}* = B\varphi_d \qquad (2)$$

If $ln\sigma_{y(rel)}*$ is plotted against volume fraction of dispersed phase, parameter B can be calculated as a line slope, with intercept in cross section of coordinate axes.

The second approach takes into account the fact that we cannot keep σ_{y0} constant, so linear correlation gives equation (3), where B is a slope and σ_{y0} can be calculated fro intercept.

$$\ln\frac{\sigma_y \cdot (1+2.5\varphi_d)}{1-\varphi_d} = B\varphi_d + \ln\sigma_{y0} \qquad (3)$$

In **Fig.4** $ln\sigma_{y(rel.)}*$ is plotted against volume fraction of dispersed phase (talc or SEBS-gMA) according to equation (2) and parameters B are determined. In **Fig.5** parameters B are determined by equation (3).
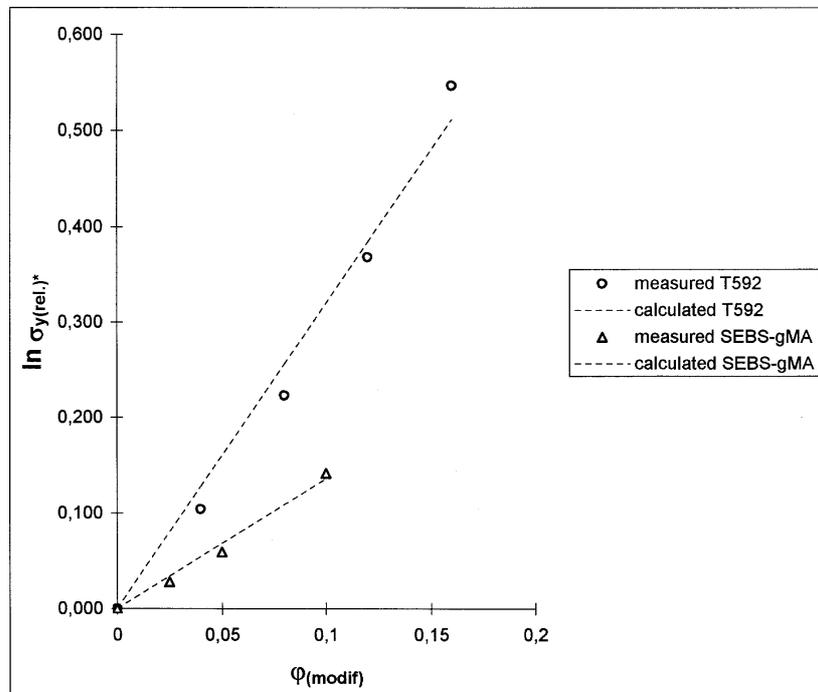
Figure 4: Dependence of linearized yield stress according to equation (2) as a function of modifier volum fraction
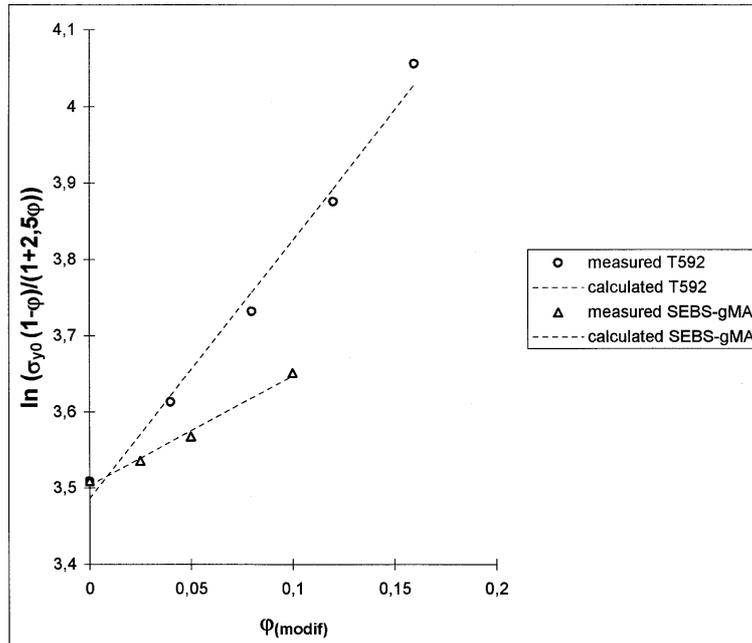
Figure 5: Dependence of linearized yield stress according to equation *(3)* as a function of modifier volum fraction

Because of different influence of polymer-filler and polymer-polymer interface on microscopic tensile behaviour, it is not possible to compare parameter *B* with blends and composites.

From calculated values of parameter *B* (**table 1**) we can see that the stress transfer between PP and talc is better than between PP and SEBS. Comparison o *B*(A20) and *B*(T592) shows that the surface treatment of talc increases stress transfer between filler and matrix; similar conclusion can be reached with *B*(SEBS) and *B*(SEBS-gMA). From measurements of σ_y, which is an interaction indicator, we can assume that higher values of elastomer content decrease interactions to matrix, probably due to coalescence, which SEM micrographs proved.

Table 1: Values of parameter *B*, determined for PP/modifier systems according to equations *(2)* and *(3)*

Modifier	*B* after eq. *(2)*	*B* after eq. *(3)*
talc (A20)	2.72	2.78
treated talc (T592)	3.20	3.39
SEBS	0.25	0.21
SEBS-gMA	1.36	1.44

The addition of talc reduces a content of ductile phase, causing yield stress to decrease. The comparison of σ_y of PP/talc and PP/treated talc composites [6] shows that the surface interactions and consequently adhesion with matrix are, in case of treated talc, stronger. At talc volume fraction above 8 % the interactions significally increase. The same conclusion is reached with binary PP/SEBS and PP/SEBS-gMA systems.

Data for σ_y of binary PP hybrid systems are being narrowly distributed around regressive curve (**Fig.6**).
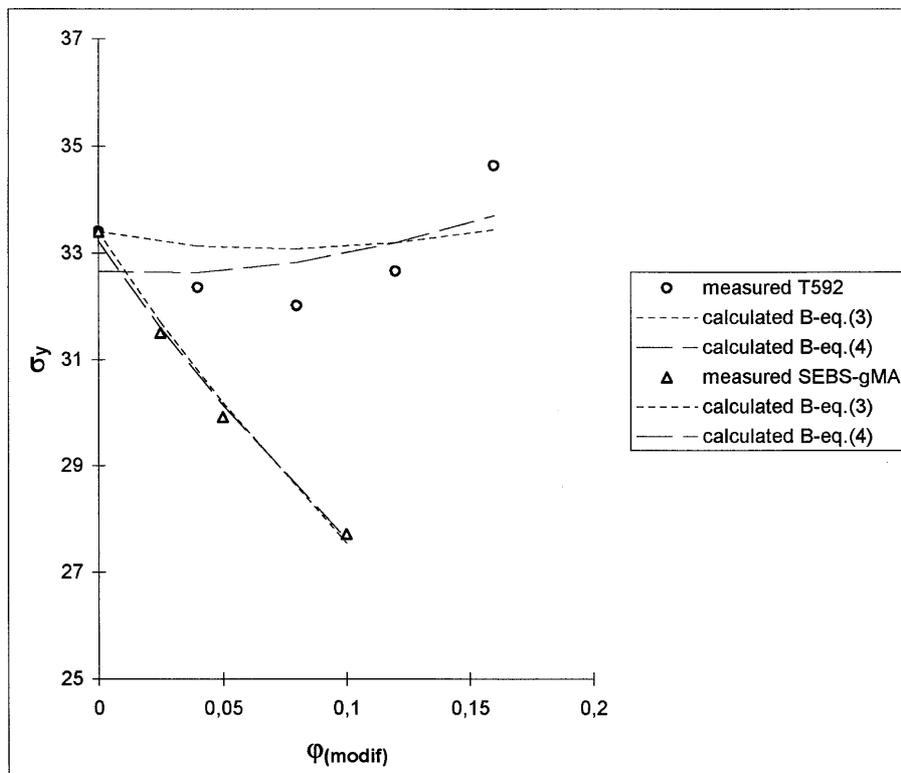
Figure 6: Comparison of calculated and measured values of yield stress for PP/T592 and PP/SEBS-gMA systems as a function of modifier (talc or elastomer) volume fraction

Stricker and Mülhaupt [2] reported that in the case of small volume fraction of dispersed phase, the yield stress of ternary hybrid composites can be calculated from independently determined parameter B:

$$\sigma_y = \sigma_{y0} \cdot \frac{1-\varphi_f}{1+2.5\varphi_f} \cdot \exp(B_f\varphi_f) \cdot \frac{1-\varphi_e{'}}{1+2.5\varphi_e{'}} \cdot \exp(B_e\varphi_e{'}) \qquad (4)$$

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where φ_f and φ_e represent a filler and elastomer volume fraction. φ_e' can be calculated by equation *(5)*.

$$\varphi_e' = \frac{\varphi_e}{1-\varphi_f} \qquad (5)$$

Equation was derived and tested on ternary PP/glass beads/SEBS composites and a good agreement between calculated and measured values was reported [2].

The yield stress of the PP hybrid composites containing SEBS slightly decreases with increasing elastomer volume fraction. In contrast to binary PP/SEBS and PP/SEBS-gMA blends ternary hybrid composites with SEBS gave much higher yield stress than SEBS-gMA, what is related to stronger interactions. Because of greater SEBS-gMA than SEBS reactivity, the opposite effect can be expected. The reason could be an uncompleted process of chemical reaction between aminosilanes and maleic anhydrid. In our future work we will be searching for parameters, resulting in higher tensile yield stress of SEBS-gMA.

Yield stress of binary and ternary PP/talc/elastomer composites have been calculated by means of equation *(4)* and the difference between measured and predicted values have been evaluated by variance (**table 2**). It was taken into account that parameters *B* were determined in two ways.

Table 2: Comparison of calculated and measured values of yield stress for binary PP/talc and PP/SEBS systems, as well as ternary PP/talc/elastomer composites with 12 vol.% of talc. Comparison were evaluated by means of variance.

Composition	Variance - used *B* eq.*(2)*	Variance - used *B* eq.*(3)*
PP/ T(A20)	0.484	0.520
PP/ T(592)	0.692	1.310
PP/ SEBS	0.025	0.024
PP/ SEBS-gMA	0.035	0.044
PP/ T(A20)/ SEBS	1.621	1.382
PP/ T(592)/ SEBS	2.470	1.415
PP/ T(592)/ SEBS-gMA	4.016	7.291

From binary composite variances, it is evident that filler and elastomer surface treatment reflects in higher values of variances which means that deviations among measured and calculated values are higher. It can also be noticed that the match between measured and calculated values, in case of binary composites, is much better than with ternary composites. For binary PP/talc composites, the use of equation *(2)* is more appropriate while for binary PP/SEBS systems both equations are equally appropriate. The prediction of yield stress for binary PP/SEBS systems with the usage of equation *(2)* is more accurate than for PP/talc composites.

A match between calculated and measured values for ternary composites when using untreated fillers and elastomers is sufficient while the interactions caused by surface treatment of fillers result in a stronger deviation to calculated values. Equation *(2)* and *(3)* both relatively well predict yield stress of ternary composites. In case o PP/T(A20)/SEBS and PP/T(592)/SEBS composites equation *(3)* has proven more efficient while equation *(2)* describes PP/T(592)/SEBS-gMA better.

Notched impact strength is, like yield stress, also an important indicator of surface adhesion. In **Fig.7**, notched Charpy impact strength is plotted against Young's modulus. The impact strength of ternary PP hybrid composites increases with elastomer volume fraction. It is unexpected that impact strength of (ternary) PP/talc composites with SEBS and SEBS-gMA are almost identical, while yield stress of (binary) composites with SEBS-gMA is even lower than those with SEBS. Owing to the chemical reaction between maleic anhydrid and aminosilane (where imid bond is formed) and consequently improved adhesion between core-shell and PP, higher values of notched impact strength of composites with SEBS-gMA could be expected. On the other hand, higher values of notched impact strength for composites with SEBS could rise due to higher parameter *B*, which is related to interfacial interactions. Due to severa parameters determining mechanical properties in ternary composites, any prediction of notched impact strength is very complicated. To achieve significant improvement in impact strength, large amounts of abou 20 vol.% of SEBS or SEBS-gMA are required [2].
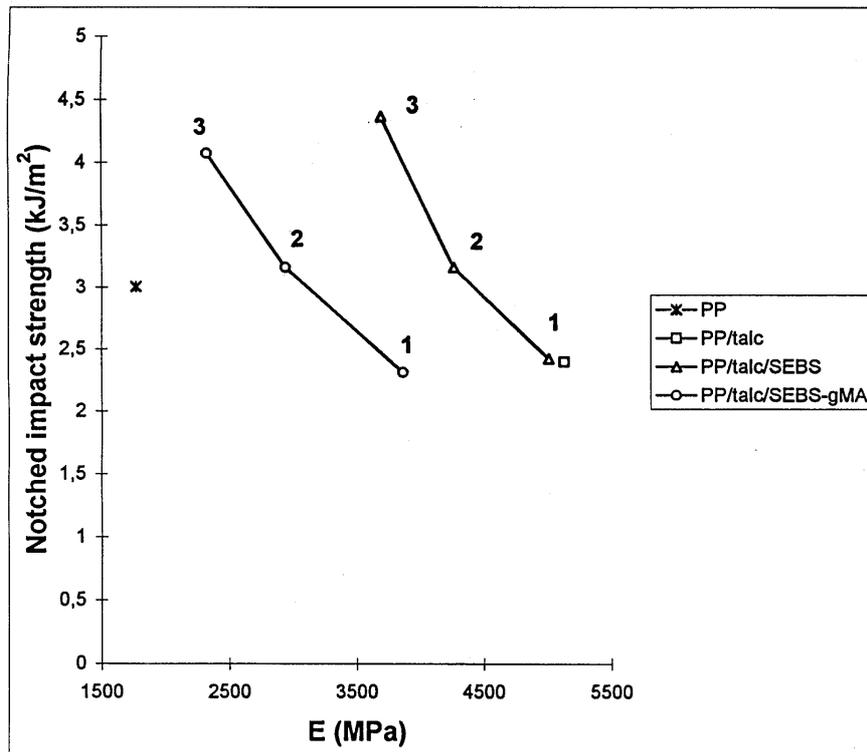
Figure 7: Notched impact strength correlated with Young's modulus for PP hybrid composites with 12 vol.% talc and with 2.5 vol.% (1), 5 vol.% (2) and 10 vol.% (3) elastomer

Conclusion

Binary PP/talc and PP/elastomer systems as well as ternary PP/untreated talc/elastomer and PP/treated talc/elastomer composites regarding to composition were investigated. Mechanical properties (Young's modulus, yield stress and notched impact strength) as well as morphology o above mentioned polymer systems were determined.

In the case of ternary PP/treated talc/SEBS composites, higher volume fraction of elastomer decreases Young's modulus. Values for composites containing SEBS are higher than those containing SEBS-gMA.

From SEM micrographs of ternary PP/treated talc/SEBS composites sufficient adhesion is depicted. At lower concentrations of elastomers up to 2.5 vol.%, SEBS is randomly dispersed in matrix, while SEBS-gMA is located on filler's surface. Concentrations o SEBS-gMA which vary from 5 to 10 vol.% leads to core-shell morphology with talc core and elastomeric shell.

In the case of ternary PP/treated talc/SEBS composites, higher volume fractions o elastomer decrease yield stress. The use of treated talc and SEBS-gMA reflects lower values of yield stress than corresponded to composites of untreated talc and SEBS. The measured values were compared to the calculated values for binary and ternary systems and a good agreement was achieved.

Notched Charpy impact strength of ternary composites reasonable increases with elastomer volume fraction. In the case of ternary PP/talc composites with SEBS or with SEBS-gMA, impact strength values were identical.

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Povzetek: Novejše raziskave so pokazale, da lahko z modifikacijo polimerne matrike s polnilom in elastomerno faz znatno vplivam na mehanske lastnosti nastalega kompozita. V raziskavah smo uporabili izotaktični PP ter ga modificirali z neobdelanim oz. obdelanim talkom in SEBS oz. SEBS-gMA. Vzorce smo pripravili preko taline v Brabenderjevem gnetilniku in stiskanjem v plošče na laboratorijski stiskalnici. Karakterizirali smo jih z merjenjem mehanskih lastnosti (Youngov modul, meja plastičnosti, zarezna udarna žilavost) in z opredelitvijo morfologije. Preučevali smo binarne sisteme sisteme PP/talk in PP/elastomer z vsebnostjo talka do 16 vol.% in do 10 vol.% elastomera, kakor tudi ternarne kompozite PP/talk/elastomer z 12 vol.% talka. Mejo plastičnosti ternarnih kompozitov smo določili še s polempiričnimi enačbami.Ugotovili smo, da uporaba obdelanih modifikatorjev (talka oz. elastomera) izboljša adhezijo z matriko, kar odseva na mehanskih lastnostih kot boljši prenos napetosti.