

## EFFECT OF FILLER TREATMENT ON THE THERMAL PROPERTIES OF COMPOSITES AND POLYMER BLENDS

E. Govorčin Bajsić<sup>1\*</sup>, V. Rek<sup>1</sup>, V. Ocelić Bulatović, B. Ormuž Pavić<sup>2</sup>

<sup>1</sup>Faculty of Chemical Engineering and Technology, Department of Polymer Engineering and Organic Chemical Technology University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia

<sup>2</sup>Ministry of Environmental Protection, Physical Planning and Construction, Ulica Republike Austrije 20, 10000 Zagreb, Croatia

\* egovor@fkit.hr

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### Abstract

*Thermoplastic composites and their blends were compounded with a twin – screw extruder and injection moulded. The effect of the addition of silane treated and untreated talc as filler on thermal properties of polymer composites and TPU/PP blends were investigated. Organosilane (3-glycidoxypopyl-metoxo silane) coupling agent was used to treat talc in order to improve the affinity relative between the filler and the composite as well as TPU/PP blends. The obtained results showed that the thermal properties of the talc filled TPU,PP composites and TPU/PP blends were improved with the addition of talc. The DMA storage modulus of the TPU/PP blends increased with the addition of talc, because the talc generated a stiffer interface in the polymer matrix. The comparison results of thermal properties among samples filled with silane treated and untreated talc filler showed that the polymer composites and TPU/PP blends filled with silane treated talc displayed the better thermal properties.*

### 1Introduction

The incorporation of fillers into thermoplastics is a fast and cheap method to reduce production costs and modify the mechanical properties. Properties of fillers play an important role in final properties of filler reinforced composites and polymer blends. Chemical properties of fillers are not varied during the melt extrusion processes, but physical characteristics such as filler shape, sizes and size distribution can be change. The filler size and distribution are very important in determining the mechanical properties (stiffness and strength) of composites. Fillers with higher surface areas will contribute to more surface contact between the filler and matrix, thus increasing the mechanical properties of the composite. Fillers with fine or small particles have higher surface areas than fillers with big particles. However, the finer the particles are, the greater their tendency is to agglomerate [1,2] and this can cause an adverse effect on mechanical properties, especially the impact resistance of composites. The reinforcement of elastomers by particulate fillers depended on the physical interactions between the filler and rubber matrix, which can determine the degree of adhesion at interface[3,4]. The surface modification of fillers by coupling agents results in an improvement of the filler-matrix interaction and provides considerable improvement in the interfacial and mechanical properties of polymer composites. Silane coupling agents have the ability to form a durable bond between organic and inorganic materials. Silane coupling agents have a general formula of  $R-(CH_2)_nSi(X)_3$ , where R group is a nonhydrolyzable

organofunctional group (amino, methacrylate, mercapto or vinyl groups) and X is a hydrolyzable group typically alkoxy,acyloxy, halogen or amine capable of interaction with fillers and polymers, respectively. Surface treatment of fillers with silane coupling agents was carried out through hydrolysis and condensation reactions as follows: initially, hydrolysis of the three labile groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with OH groups of the substrate. Finally during drying or curing, a covalent linkage is formed with the substrate with concomitant loss of water. Although described sequentially, this reaction can occur simultaneously after the initial hydrolysis step. At the interface, there is usually only one bond from each silicon of the organosilane to the substrate surface. The two remaining silanol groups are present either in condensed or free form. The R group remains available for covalent reaction or physical interaction with other phases. Polyurethane can be effectively coupled with two types of silanes. The first type, including isocyanate functional silanes, may be used to treat the filler directly or integrally blended with the diisocyanate. Amine and alkanolamine functional silanes are blended with polyol rather than the diisocyanate. Isocyanate functional silanes couple with the polyol. Alkanolamine functional silanes react with the isocyanate to form urethane linkages, while amine silanes react with the isocyanates to yield urea linkages [5]. In this paper, the effect of silane treated and untreated-talc on the thermal properties of composites and polymer blends is investigated.

## 2 Materials and testing methods

### 2.1 Materials

The characteristics of PP, talc, and silane used in this work are summarized in Table 1.

Material	Trade name	Supplier	MFI	d (g/cm <sup>3</sup> )	Shape
i-PP	Moplen 500N	Basell	12 (g/ 10 min) at 190°C	-	Pallet
TPU	Desmopan 588E	Bayer	-	-	Pallet
Talc	Luzenac 20MO	Solvay	-	2.8	Powder

MFI-melt flow indeks; d-density

**Table 1.** Material specifications.

The detailed compositions of the talc filled composites and blends are summarized in Table 2.

A 3-glyclodioksy-propyltrimethoksyasilane was used for surface treatment of talc, for complete surface wetting the following amounts were required: 200 cm<sup>3</sup> of methanol, 300 cm<sup>3</sup> water, 2-3 drops of sulphuric acid and 30 cm<sup>3</sup> of silane. After the wetting process talc was dried in an oven for 24h at 110°C . Thermoplastic polyurethane (TPU) and polypropylene (PP) were mixed with talc content of 5 wt.%. Two series of different TPU,PP composites and blends were prepared by melt blending using a Rondol 21mm LAB TWIN twin-screw extruder, one with untreated talc (TPU/PP/T blends) , the other with silane-treated talc (TPU/PP/T (GPTMS) blends) (Table 2), the temperature profile from hopper to die was as follows:170 °C, 180 °C, 180 °C, 200 °C, 200 °C and 200 °C. Test specimens were injection moulded in a injection press (Rondol , High Force 5 ) at 180°C.

Composites and blends	Composites and blends with untreated talc	Composites and blends treated with 3-glyclodioksypropyltrimethoksysilane (GPTMS)
TPU	TPU/T	TPU/T (GPTMS)
PP	PP/T	PP/T /GPTMS)
TPU/PP 80/20	TPU/PP/T 80/20/5	TPU/PP/T (GPTMS) 80/20/5
TPU/PP 50/50	TPU/PP/T 50/50/5	TPU/PP/T (GPTMS) 50/50/5
TPU/PP 20/80	TPU/PP/T 20/80/5	TPU/PP/T (GPTMS) 20/80/5

**Table 2.** The composition of TPU, PP composites and blends.

## 2.1 Testing methods

### 2.1.1 Differential scanning calorimetry (DSC)

DSC measurements were performed with the DSC Mettler Toledo DSC 822<sup>e</sup> under nitrogen flow (40 ml/min) for melting and crystallization transitions. The samples were heated up to 190°C at a heating rate of 10°C/min and held there for 10 min in order to eliminate any previous thermal history. Then, the samples were cooled with liquid nitrogen to -100 °C and heating to 190°C. The cell constant was calibrated using a standard indium sample.

### 2.1.2 Dynamic mechanical analysis (DMA)

Dynamic mechanical measurements were performed with a TA Instruments model DMA 983 Analyzer, over the temperature range of -100 to 250°C at a frequency of 1 Hz and a heating rate of 5°C min<sup>-1</sup> on samples in the form of injection molded bars (20,00 x 12,00 x 3,00 mm). All the samples were cooled to -100°C using liquid nitrogen.

## 3 Results and discussion

### 3.1 Differential Scanning Calorimetry (DSC)

The DSC curves of second heating show two melting endotherms of the hard segments in the neat TPU, one associated with the dissociation of short - range order in the hard segment domains (endo I) and the other associated with melting of long - range order in the hard segment domains (endo II) [Fig. 1, Table 3], while the second DSC heating of untreated and silane treated talc (TPU/T composite) give three endotherms: endo I, endo II and endo III associated with melting of the microcrystalline regions in the hard segment domains [6-8]. The melting temperature and enthalpy of second heating of silane treated talc (TPU/T (GPTMS) composite) increase in comparison with  $T_m$  of the neat TPU and untreated-talc TPU/T composite. The increase in these temperatures could be attributed to the activity of the filler which is higher in the TPU/T(GPTMS) composites; the nucleating effect increasing with the presence of silanes. In this sense, the treated talc is more active. The second heating and cooling curves of PP and PP-talc composite are shown in Figure 2a and 2b, respectively, thermal properties are summarized in Table 3. The second DSC heating run of the neat PP and PP/T composites shows a melting endotherm related to the  $\alpha$  phase (monoclinic) of PP [9-11] . The DSC cooling curve revealed a sharp exothermic crystallization peak ( $T_c$ ), according to the results compiled in Table 3, the  $T_c$  for the PP/T composites is in the following manner:  $T_c$  (PP/T (GPTMS) 100/5) >  $T_c$  (PP/T 100/5) >  $T_c$  (PP 100/0). The crystallinity,  $\chi_c$ , of PP is calculated using a value of  $\Delta H_m$  for completely crystalline PP,

equal to 165 J/g [12, 13]. The degree of crystallinity ( $\chi_c$ ) of PP/T composites (Table 3), decreases in the order:  $\chi_c(\text{PP/T(GPTMS)} 100/5) > \chi_c(\text{PP/T } 100/5) > \chi_c(\text{PP } 100/0)$ . The crystallinity increased by the treatment of talc with silane [14].

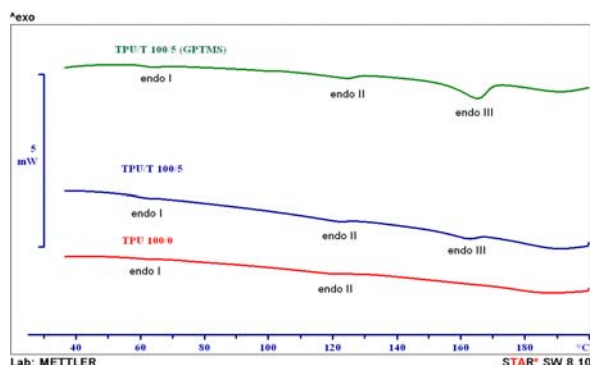


Figure 1. DSC melting curves of the neat TPU, untreated and silane treated talc TPU/T composite.

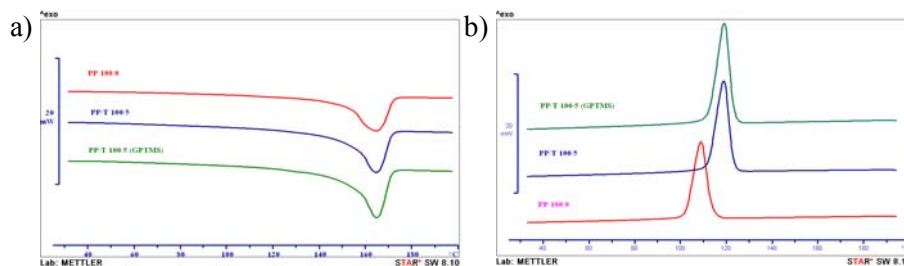


Figure 2. DSC melting (a) and cooling (b) curves of the neat PP, untreated and silane treated talc PP/T composite.

Figure 3 (a)-(c) show the influence of the surface treatment on the crystallization behavior of the investigated TPU/PP blends. The results are reported in Table 3. In the TPU/PP 80/20 blends three exothermic crystallization peaks are observed, that is, crystallization temperature,  $T_c$ , of PP at 110.0°C and two peaks at 76.3°C and 46.3°C corresponding to the crystallization of the hard segments crystallites in TPU. The crystallization temperatures are higher in the silane treated talc (TPU/PP 80/20 blend) than unfilled and talc-filled blends. Alonso et al. [15] showed that the orientation of talc particles was higher when the filler was treated with silanes. DSC cooling curves of TPU/PP 50/50 and TPU/PP 20/80 blends exhibited only one exothermic peak corresponding to the  $T_c$  values of the PP. From the results obtained, the crystallization temperatures and crystallinity increased by the treatment of talc with silane when compared with unfilled and talc filled TPU/PP blends. These results suggest that the adding of treated talc in TPU/PP blends the adhesion between the polymer and talc is improved when the talc is treated with silane.

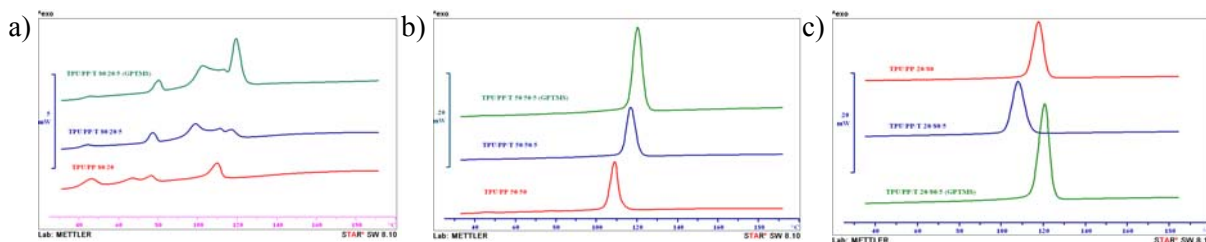
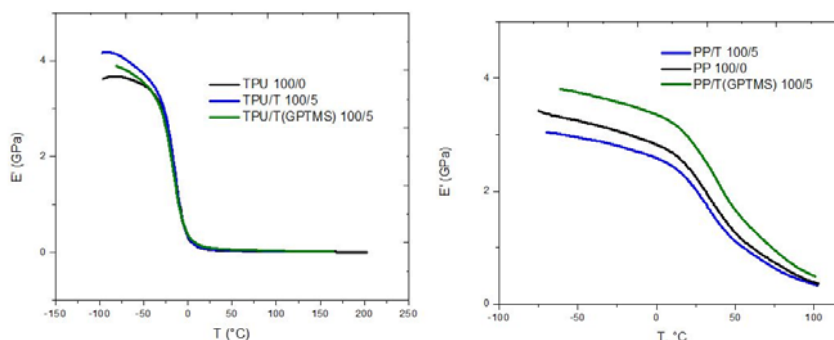


Figure 3. DSC crystallization curves of TPU/PP 80/20 (a), TPU/PP 50/50 (b) and TPU/PP 20/80 (c) blends .

Composite /Blends	T <sub>mTPU</sub> (°C)	T <sub>mPP</sub> (°C)	T <sub>cPP</sub> (°C)	χ <sub>c</sub> (%)
TPU 100/0	60.9; 118.0	-	-	-
TPU/T 100/5	61.7; 124.0; 161.8	-	-	-
TPU/T(GPTMS) 100/5	64.1; 124.0; 164.7	-	-	-
PP 100/0	-	164.2	109.6	37.4
PP/T 100/5	-	164.1	119.8	39.5
PP/T(GPTMS) 100/5	-	164.0	120.1	43.4
TPU/PP 80/20	-	161.7	110.0	7.0
TPU/PP/T 80/20/5	-	162.2	99.0	7.7
TPU/PP/T(GPTMS) 80/20/5	-	164.8	119.5	13.8
TPU/PP 50/50	-	162.8	109.8	19.6
TPU/PP/T 50/50/5	-	160.8	117.6	23.0
TPU/PP/T(GPTMS) 50/50/5	-	164.6	121.2	36.0
TPU/PP 20/80	-	163.8	118.4	29.3
TPU/PP/T 20/80/5	-	164.1	108.7	29.6
TPU/PP/T(GPTMS) 20/80/5	-	166.8	121.6	42.5

**Table 3.** Thermal properties of the neat TPU, PP, TPU/T, PP/T composites and TPU/PP blends.

The viscoelastic properties of the neat TPU, PP; TPU/T, PP/T composites and TPU/PP blends were characterized by means of dynamic mechanical analysis (DMA). The glass transition temperature ( $T_g$ ) of soft segment of the neat TPU [16,17] observed at  $-14.2^\circ\text{C}$ , for untreated talc TPU composite (TPU/T) at  $-13.6^\circ\text{C}$  and at  $-15.9^\circ\text{C}$  when the talc is treated with silane (TPU/T (GPTMS) composite), Table 4. The presence of untreated talc restricted the mobility of molecular chain of TPU, and so  $T_g$  increases as a consequence of interactions between talc and the TPU chains. The decrease of  $T_g$  in the case of TPU/T (GPTMS) composite may be attributed to the weak filler -soft segment interaction. In the case of the neat PP, PP/T (untreated) and PP/T (treated) composites three distinct relaxations were observed (Table 4). The glass transition ( $T_g$ ) of the PP amorphous phase at  $29.5^\circ\text{C}$  [18], at  $-19.2^\circ\text{C}$  the  $\gamma$ -relaxation of the PP appears associated with the motions of small-chain groups like methyl and methylene [19] and another relaxation at higher temperatures appears,  $\alpha_C$  relaxation shoulder, (at approximately  $84.4^\circ\text{C}$ ) and could be related to a more rigid chains with amorphous character related to the PP crystallites (tie molecules etc.). According to the results included in Table 4:  $T_g$  (PP/T(GPTMS) 100/5) >  $T_g$  (PP) >  $T_g$  (PP/T 100/5). Figure 4 shows curves of the storage modulus ( $E'$ ) for the neat TPU and TPU/T composites, the storage modulus is almost unaffected by the talc filling. The PP/T (GPTMS) composite have a higher storage modulus than the untreated talc PP composite (PP/T 100/5). In the surface treated talc filled composite the nucleating effect of the talc increasing with the presence of silane and the interface will be stiffer (Figure 4, Table 4).



**Figure 4.** Plot of storage modulus ( $E'$ ) of the neat TPU, PP, untreated and silane treated talc TPU/T and PP/T composite.

From table 4, it can be seen that in all investigated TPU/PP blends the values of  $T_g$  were shifted to higher temperatures as the content of PP increase and with the addition of untreated and treated talc, when compare with the neat TPU. The increase in  $T_g$  in the TPU/PP/T (treated) blends may be attributed to increased polymer-filler-polymer interaction.

Figure 5 shows the temperature dependence of the storage modulus,  $E'$ , for all investigated unfilled, talc-filled and silane treated talc TPU/PP blends. The results are listed in Table 4. The storage modulus increase with adding the silane treated talc because of the improved adhesion between the polymer and talc in the presence of silane, the interaction between the talc and polymer was higher.

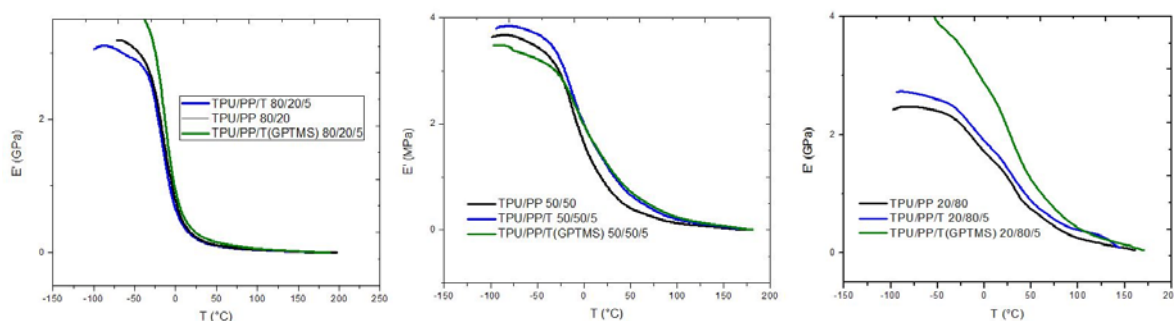


Figure 5. Plot of storage modulus ( $E'$ ) of TPU/PP 80/20, TPU/PP 50/50 and TPU/PP 20/80 blends.

Composite /Blends	$T_{gTPU}$ , °C	$T_{gPP}$ , °C	$\alpha_C$ , °C	$\gamma$ , °C
TPU 100/0	-14.2	-	-	-
TPU/T 100/5	-13.6	-	-	-
TPU/T(GPTMS) 100/5	-15.9	-	-	-
PP 100/0	-	29.5	84.4	-19.2
PP/T 100/5	-	28.8	87.7	-29.4
PP/T(GPTMS) 100/5	-	34.7	63.0	-24.9
TPU/PP 80/20	-14.5	-	-	-
TPU/PP/T 80/20/5	-14.6	-	-	-
TPU/PP/T(GPTMS) 80/20/5	-12.6	-	-	-
TPU/PP 50/50	-8.9	-	83.9	-
TPU/PP/T 50/50/5	-13.1	25.9	82.9	-
TPU/PP/T(GPTMS) 50/50/5	-12.6	18.1	-	-
TPU/PP 20/80	-10.3	26.4	74.3	-
TPU/PP/T 20/80/5	-9.9	26.7	85.9	-
TPU/PP/T(GPTMS) 20/80/5	-8.9	25.1	79.4	-

Table 4. DMA results of the neat TPU, PP, TPU/T, PP/T composites and TPU/PP blends

#### 4 Conclusions

The melting temperature and enthalpy of silane treated talc (TPU/T (GPTMS) composite) increase. This behavior could be attributed to the activity of the filler which is higher in the TPU/T (GPTMS). The degree of crystallinity ( $\chi_c$ ) of PP/T composites increased by the treatment of talc with silanes. The crystallization temperatures and crystallinity increased in TPU/PP blends by the treatment of talc with silane because of the improved adhesion between the polymer and the treated talc. The decrease of  $T_g$  in the case of TPU/T (GPTMS) composite may be attributed to the weak filler-soft segment interaction. The  $T_g$  of the PP amorphous phase increased in the PP/T(GPTMS) composite. In the TPU/T composites the storage modulus is almost unaffected by the talc filling, while in the PP/T (GPTMS) composite storage modulus increased. The increase in  $T_g$  in the TPU/PP/T (treated) blends may be attributed to increased polymer-filler-polymer interaction. The storage modulus

increase with adding the silane treated talc in all investigated TPU/PP blends because of the higher interaction between the talc and polymer.

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