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TPU/MICA COMPOSITES PREPARED IN TORQUE RHEOMETER: PROCESSABILITY, MECHANICAL PROPERTIES AND MORPHOLOGY

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Abstract. This work is concerned with the preparation of thermoplastic polyurethane elastomer (TPU) composites with mica, and their characterization as for processability, mechanical and thermal properties and morphology behavior. The amount of added mica varied from 0 to 20 phr and the results showed few interactions between mica and the polymer matrix. Processability is facilitated by the increasing amount of mica but TPU upon strain crystallizability, as well as T_g , decrease with the increase in mica content. The main interest in using mica is the evaluation of a low cost mineral as a reinforcing material for the engineering polymer TPU.

Keywords: thermoplastic polyurethane elastomer, mica, processability, mechanical properties, morphology.

1. Introduction

Thermoplastic polyurethane (TPU) is one of the most versatile engineering thermoplastics which can be tailored to meet the diversified demands of modern technologies in different fields such as coatings, adhesives, reaction molding plastics, fibers, foams, rubbers, thermoplastic elastomers, and composites [1].

In comparison to conventional rubbers TPU possesses high tensile modulus, high abrasion resistance, and high wear and tear resistances. It is well known that TPU elastomers are linear multi-block copolymers containing soft and hard segments. The hydrogen bonds existing in TPU are labile, and thus they can be redistributed depending on thermal effects or by means of modification. The hydrogen bonds distribution influences the extent of microphase separation as well as the set of properties typical of these materials [2]. In providing a network of physical junctions, the hydrogen bonds in TPU play a critical role.

Solid minerals such as micas have a high surface energy, due to the presence of hydroxyl groups on the surface. Because of this feature, polar polymers such as polyurethane polyether could be thought of as being able to form H-bonds with the hydroxyls available on the filler surface [3].

In the present study attempts have been made to use particulate mica as a filler for TPU, with the objective to investigate the potential of this mineral in bringing about improvements in processability and also the effects this filler would have on the properties of the final compound [4]. Mica muscovite, a plate-like crystalline aluminum silicate, was used in these composites due to its excellent mechanical, electrical and thermal properties as well as to its low cost and abundance in Brazil [5]. In this work, the amount of mica ranged from 0 to 20 phr.

2. Experimental

2.1. Materials

Thermoplastic Polyurethane Elastomer (TPU), a poly ether type, with the molecular weight $M_n = 69000$ g/mol, $M_w = 220000$ g/mol and PD (M_w/M_n) = 3.2, was supplied by Basf S.A. (SP, Brazil); mica muscovite ($K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$), from Brasilminas Indústria e Comércio Ltda. SP, Brazil, presented the characteristics: density 2.78 g/cm³, superficial area 7.575 m²/g and particle size distribution from 50 to 0.2 μ m (obtained by Sedigraph 5100 with software Micrometic V1.02).

2.2. Preparation and Processability of Composites

Mixing was performed on a Rheomix 600 Haake rheometer mixing chamber, during 30 min at 453 K and 60 rpm, with a roller type rotor. The amount of mica in the

TPU composites varied from 0 to 20 phr (parts per hundred parts of resin).

From a torque *versus* time curve the following parameters were measured: totalized torque (TTQ), given by the integral under the curve, and stabilized torque (TQ), the equilibrium torque which indicates that homogeneity has been achieved, and can be considered as the melt viscosity. The mechanical energy required to process the mixtures (E_M) can be calculated, multiplying TTQ by the angular velocity w ($w = 2p$ rpm). The specific energy of processing (E_{sp}) is obtained from E_M as a function of the material mass inside the mixing chamber ($E_{sp} = E_M/g$). The equations can be found in the literature [6-9].

2.3. Characterization

2.3.1. Mechanical properties

The tensile strength properties were measured on an EMIC DL3000 with a clamp speed of 200 mm/min, according to DIN 53504 standard. Specimens were of S2 type. Shore A hardness was determined following ASTM D 2240 procedure, and abrasion resistance was carried out according to DIN 53516, in a Bareiss AB6026/03 Abrasimeter using weight of 10 N and distance of 40 m.

2.3.2. Transmission electron microscopy (TEM)

A Zeiss CEM 902 transmission electron microscope was utilized to investigate the morphology of the TPU/mica samples. The voltage was of 80 kV.

2.3.3. Differential scanning calorimetry (DSC)

The glass transition temperature (T_g) was determined in a Differential Scanning Calorimeter (DSC), model Q 1000, from TA Instruments, under nitrogen atmosphere, temperature ranging from 153 to 473 K and 10 K/min (10 K/min) heating rate. After the first run, the samples were fast cooled to 153 K and reheated at the same heating rate. T_g was taken from the second run.

3. Results and Discussion

If a polymer is introduced into the mixing chamber of the Haake torque rheometer, the solid granules offer at first a

certain resistance to the free rotation of the blades and therefore the torque increases. After this resistance is overcome, the torque is required to rotate the blades at the fixed speed decreases, and then reaches a steady-state after a short time. When the heat transfer has been achieved so that the particles core is completely melted, the torque decreases again and reaches a second steady-state regime [10]. This last steady-state torque is a measure of the melt viscosity (stabilized torque – TQ) for a given morphology under certain experimental conditions. In Table 1 results of processability parameters obtained in the Rheomix Haake rheometer for all developed compositions are shown.

The stable condition, determined from the stabilization time was considered after discontinuation of mixing, undertaken to prevent risks of further degradation of the mixture components. The processability results show that in addition to mica the stabilized torque decreases. As mica is a plate like material [5] its crystalline form may facilitate the flow of these TPU composites, thus acting as a processing agent. As a consequence, totalized torque (TTQ), mechanical energy (E_M) and specific energy (E_{sp}) all decrease with the increase in the filler content. These results are very interesting from the technological point of view, as larger quantities of composites can be produced per unit of time.

As said earlier, mica has a high surface energy, due to presence of hydroxyl groups on the surface. Polar polymers as polyurethanes polyether may then be able to form H-bonds with the hydroxyls available on the filler surface [3], in such a way that the final properties of the compound will be influenced by the type of processing.

This influence has already been observed, as described in a previous work [11], for TPU-mica composites obtained by extrusion. In the present work processing in a mixing chamber was specially chosen as to minimize the effects caused by the interactions that may occur during processing, which would induce molecular organization. Fig. 1 shows the stress *versus* strain results for all composites.

From Fig. 1 it can be seen that the stress induced orientation starts near 400 % strain. At higher strains (beyond 600 %) the resistance decreases and the elongation at break undergoes a little decrease with the increasing addition of mica.

Table 1

Processability results from Rheomix Haake rheometer

Composites TPU/Mica, phr	Stabilized torque (TQ), Nm	Totalized torque (TTQ), J · min	Mechanical energy (E_M), kJ	Specific energy (E_{sp}), J/g
100 / 0	2.31	137.00	51.62	954.16
100 / 5	2.16	112.65	42.45	762.53
100 / 10	1.65	110.59	41.68	728.67
100 / 15	1.40	107.00	40.32	687.35
100 / 20	1.00	98.00	36.93	614.78

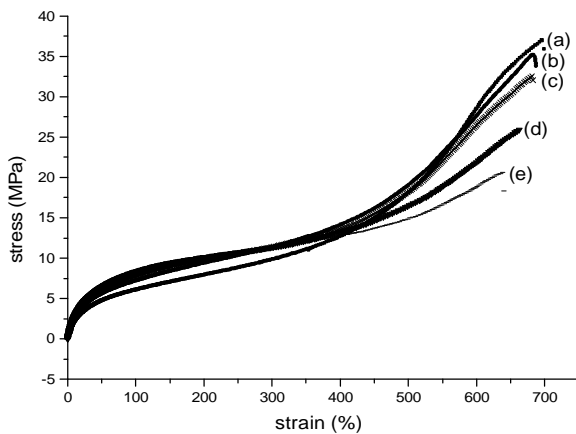


Fig. 1. Stress-strain curves of TPU polyether and its composites with mica: TPU 100/0 (a), TPU 100/5 phr mica (b), TPU 100/10 phr mica (c), TPU 100/15 phr mica (d) and TPU 100/20 phr mica (e)

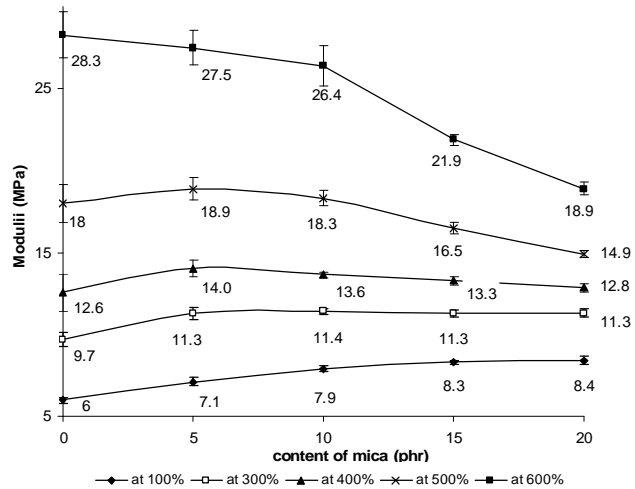


Fig.2. Moduli of TPU composites with mica

Table 2
Results of mechanical properties of TPU/mica composites

Composites TPU/Mica, phr	Tensile strength, MPa	Elongation at break, %	Energy at break, N·mm	Abrasion loss, mm ³
100/0	36.88 ± 2.82	697 ± 66	17666	14.26 ± 1.11
100/5	35.11 ± 4.41	686 ± 62	16813	24.39 ± 1.26
100/10	32.51 ± 2.33	682 ± 40	16739	35.12 ± 1.45
100/15	25.86 ± 1.94	659 ± 25	14051	46.22 ± 0.77
100/20	20.61 ± 2.69	635 ± 69	12478	56.41 ± 3.00

Tensile parameters are dependent on the chains orientation during the applied stress. As the composites in this work were not extruded, but rather obtained in a mixing chamber, orientation of the TPU chains was not favoured by the used processing technique. According to D. Gan *et al.* [3] the effect of the filler on the tensile strength may be also attributed to the counterbalance of two phenomena, as increasing filler contents is present in the polymer composites, namely, the increased effective surface fracture energy, and the increased sizes of voids and agglomeration of filler particles [12, 13]. At the addition of the filler to the polymer matrix, dispersed particles make the crack propagation path longer, absorb a portion of the energy and enhance the plastic deformation. Therefore, the surface fracture energy increases and the strength of the composites should also increase with the volume percentage of the filler [12]. On the other hand, by increasing the filler contents, the size of the voids formed when the polymer matrix becomes detached from the filler particles due to deformation, will become critically large and may initiate

the main crack [12]. Furthermore, the inevitably increased agglomeration of dispersed filler particles will result in decreased mechanical strength due to the low strength of the agglomerates themselves [13].

Table 2 shows that the rupture energy decreases with the increasing amount of mica, which can be a consequence of the wide distribution of particle sizes, thus making feasible the possibility of clusters formation.

These clusters would hinder the TPU soft segments from becoming oriented under tension. Similar behaviors have been reported in the literature with TPU composites using other fillers [14, 15].

The results of modulus at different strains as a function of mica content can be better visualized in Fig. 2.

At very low strain, mica contents up to 20 phr cause this property to increase as a consequence of TPU-filler interactions. These interactions although not numerous, are still enough to impart a little stiffness to the material at this level of deformation. However, at very high strain (600 %) these interactions are no longer able to be maintained and

the composites come to fail, also as a consequence of the processing method (mixing chamber).

Fig. 3 shows the results for all composites Shore A hardness .

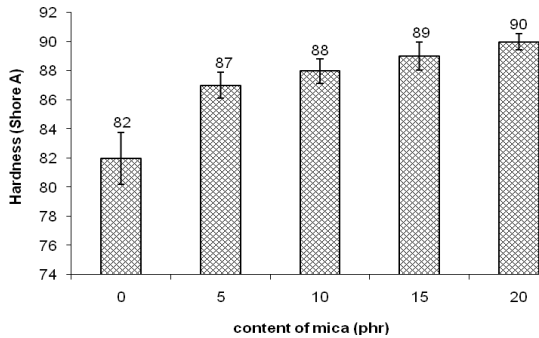


Fig. 3. Hardness of TPU composites with mica

This property increases with the addition of mica, as a consequence of increasing molecular stiffness, thus corroborating the modulus behavior at a low stress.

The friction and abrasion of polymer materials are complex and dynamic processes, closely related to

hardness, toughness, fatigue, and so on. TPUs are materials with excellent abrasion resistance and high resilience. As a result of these properties, they have been widely used in the manufacturing of oil and water pipes. In this work, abrasion resistance of the composites decreased as the amount of the particulate filler increased, as shown in Table 2, since mica particles are much easier to be removed from the composite surface than the polymer.

The dispersion of mica particles in the TPU matrix was observed by transmission electron microscopy (TEM). Fig. 4 shows the micrographs of TPU composites with 5 and 10 phr of mica, at 2 μm scale and details at 500 nm.

The used mica has a wide distribution of particle sizes (50 to 0.2 μm) and from the micrographs this large size dispersion can be observed. Also it can be noticed that the particle sizes are kept unchanged, as expected, since their incorporation was carried out in a mixing chamber, under low shear.

Fig. 5 shows the variation of the glass transition temperature (T_g) values for the TPU soft segments, obtained from DSC curves, as a function of mica content.

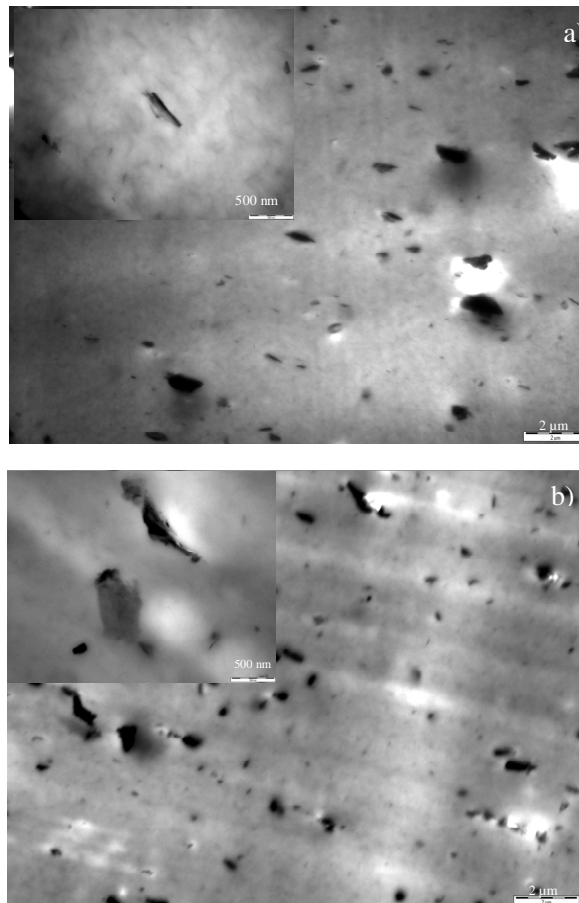


Fig. 4. TEM microphotograph of TPU polyether/ mica composites: TPU/ 5 phr of mica (a) and TPU/ 10 phr of mica (b)

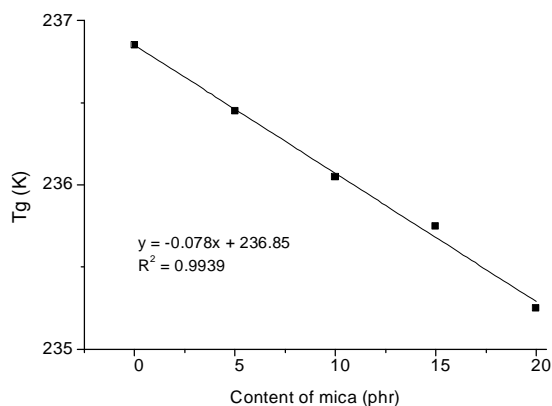


Fig. 5. Variation of the glass transition temperature (T_g) with the content of mica

The T_g depends on chain flexibility, intermolecular attraction, steric effects, molecular weight and so forth. When the chain flexibility of the polymer increases, T_g decreases [16]. In the present case, the values of T_g for the TPU/mica composites show a linear (correlation coefficient of 0.9939) decrease as higher amounts of mica are added. As said earlier in this work, the hydroxyl groups placed on the surface of mica are able to develop interactions, through hydrogen bonding, with the urethane groups which are mostly situated in the hard segments phase. The development of these interactions will cause the chains to move apart from each other leaving larger free volumes for the movements of the flexible segments, thus decreasing T_g .

4. Conclusions

In this work, the incorporation of mica into TPU was carried out in a mixing chamber so as to minimize processing effects that could induce molecular organization of any kind. In spite of this, from the results of processability, glass transition temperature and tensile modulus, small interactions between mica and the polymeric matrix have been observed. The presence of filler agglomerates, mainly at mica contents above 10 phr, may be responsible for the reduction in the abrasion and stress resistances as these larger particles will prevent the polymer to crystallize under stress.

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References

- [1] Moon S.-Y., Kim J.-K., Nah C. and Lee Y.-S.: Eur. Polym. J., 2004, **40**, 1615.
- [2] Wang X. and Luo X.: *ibid*, 2391.
- [3] Gan D., Lu S., Song C. and Wang Z.: Eur. Polym. J., 2001, **37**, 1359.
- [4] Vainio M., Heino M. and Seppala J.: Polymer, 1998, **39**, 865.
- [5] Miles I. and Rostami S.: Multicomponent Polymer Systems. Wiley, New York 1992.
- [6] Haake Laboratory Information 9002-7E, Haake Mess-Technic GmbH, Germany, 1989.
- [7] Lapa V., Visconte L., Affonso J. and Nunes R.: Polym. Test., 2002, **21**, 443.
- [8] Gonzalez E., Costa D., Visconte L. and Nunes R.: Polym. Test., 2001, **20**, 703.
- [9] Escocio V., Visconte L., Nunes R. and Oliveira M.: Int. J. Polym. Mater., 2008, **57**, 374.
- [10] Freire E., Bianchi O., Monteiro E. *et al.*: Mater. Sci. Eng., 2009, **C29**, 657.
- [11] Pinto U., Visconte L. and Nunes R.: Eur. Polym. J., 2001, **37**, 1935.
- [12] Berlin A., Volfson S., Enikolopian N. and Negmatov S.: Principles of Polymer Composites. Springer, Berlin 1986.
- [13] Nielsen L.: Mechanical Properties of Polymers and Composites. Marcel Dekker, New York 1974.
- [14] Nunes R., Fonseca J. and Pereira M.: Polym. Test., 2000, **19**, 93.
- [15] Nguyen D., Lee Y., Raghu A. *et al.*: Polym. Int., 2009, **58**, 412.
- [16] Seo W., Sung Y., Han S. *et al.*: J. Appl. Polym. Sci., 2006, **101**, 2879.

ПРИГОТУВАННЯ КОМПОЗИТІВ ТПУ/СЛЮДА В КРУТИЛЬНОМУ РЕОМЕТРІ: ТЕХНОЛОГІЧНІСТЬ, МЕХАНІЧНІ ВЛАСТИВОСТІ ТА МОРФОЛОГІЯ

Анотація. Описаний процес підготовки композитів термопластичного поліуретанового еластомеру (ТПУ) з слюдою, та наведені такі їх характеристики, як технологічність, механічні та теплові властивості і морфологія. Кількість доданої слюди змінювалась від 0 до 20 мас.част. Показана взаємодія між слюдою і полімерною матрицею. Встановлено, що збільшення кількості слюди сприяє технологічності процесу, але при цьому зменшується напруження кристалізованості та температура склування. Показано, що низька вартість мінералу як укріплюючого матеріалу для технічного полімеру ТПУ є критерієм оцінювання.

Ключові слова: термопластичний поліуретановий еластомер, слюда, технологічність, механічні властивості, морфологія.