

Properties and Preparation of Thermoplastic Polyurethane/Silica Hybrid Using Sol–Gel Process

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Received 1 June 2004; accepted 14 November 2004

DOI 10.1002/app.21833

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A thermoplastic polyurethane elastomer/silica hybrid (TPU/SiO₂) was prepared using the sol–gel process. This work was undertaken to investigate the thermal and physical properties of this type of hybrid by employing different catalyst systems during sol–gel processing. Two types of catalyst systems including acetic acid (HOAc) and hydrochloric acid (HCl) were used to prepare sol particles. The mixing of the sol solution and TPU solution was then carried out to form a TPU/silica hybrid. Fourier transform IR spectra and dynamic mechanical properties were recorded to depict the enhanced interfacial interaction. Thermogravimetric analysis was used to determine the actual silica content forming in the hybrid and to evaluate the heat resistance of the hybrid. Mechanical properties such as the

tensile strength and cutting strength were investigated at various concentrations of *in situ* silica. The tensile strength increased at all concentrations of silica. In contrast, the cutting strength decreased, probably because of a reduction of the energy dissipation from silica as physical crosslinks. The HOAc catalyzed system showed better optical properties than the HCl catalyzed system. The fracture surface was revealed through scanning electron microscopy to observe the degree of dispersion of SiO₂, which in turn confirmed the results for the optical and mechanical properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1316–1325, 2005

Key words: thermoplastic polyurethane; silica; hybrid; nanocomposite; sol–gel

INTRODUCTION

Polymer composites featuring both stiffness and strength have been of great commercial interest in the past decade. Conventional polymer composites generally are directly formed through a simple blend of pristine polymer and inorganic filler. However, phase separation on the order of a few microns often occurs because of a lack of substantial interaction between the dispersed filler and polymer matrix. Recently, an organic–inorganic hybrid with a nanostructure (termed nanocomposite) has been developed through nanotechnology. Nanocomposites have received much attention recently because of their outstanding optical, electrical, and mechanical properties, and so forth. One of the most widely used routes offering the merits of a low processing temperature with energy savings is using the sol–gel method to prepare nanocomposites.

Geffcken and Berger prepared an inorganic oxide film through condensation of nanoparticles using the sol–gel approach in 1939.¹ The sol–gel method became popular in the ceramics industry around the

mid-1970s, and various types of inorganic glass were manufactured based on this approach.² Philipp and Schmidt³ and Wilkes et al.⁴ carried out pioneer works on the preparation of organically modified silicate (Ormocil or CERAMER) using various types of alkoxysilane via the sol–gel process. Since then, numerous studies have focused on the preparation of new types of hybrids. Factors affecting the final performance of the products include the water/silane ratio, catalyst, reaction temperature, and so forth.⁵

In such nanocomposites, the interfacial interaction between the polymer matrix and dispersed silicate layers is a crucial factor to attain their unique properties. Unfortunately, strong silanol (Si–OH) interactions between silicate layers often prevent a fine dispersion of silica particulate into the polymer matrix. Approaches to overcome this problem have been widely studied in academia and industry. Novel nanoscale hybrids using the sol–gel process include polystyrene,⁶ poly(methyl methacrylate),⁷ polyimide,⁸ poly(tetramethylene oxide),⁹ poly(dimethyl siloxane),¹⁰ styrene–butadiene–styrene block copolymer (SBS),¹¹ and so forth. Mark has conducted an extensive review on those ceramic reinforced polymer nanocomposites.¹²

Among those nanocomposites, there are only limited elastomers being discussed except poly(dimethyl siloxane). Taking another elastomeric material as an

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example, highly dispersed SiO₂ has been incorporated into styrene-butadiene rubber (SBR) to successfully improve the wear resistance, wet traction, and low rolling resistance of tire compounds, which is termed green tire technology.¹³ Although the properties of rubbery materials have been enhanced through this approach, environmental issues still remain to be resolved. Thermoplastic elastomers (TPEs) generally possess elastomeric characteristics, yet they can be efficiently processed as thermoplastics. Because of this advantage over conventional rubber, the annual growth rate of TPEs has reached 7%.¹⁴ It is interesting to see if the performance of a TPE/silica hybrid may be further upgraded using the sol-gel process.

Chen et al.¹¹ investigated the physical properties of an SBS/SiO₂ hybrid prepared using the sol-gel approach. They concluded that the heat resistance and storage modulus both increased. An optimal value was attained at a dosage of 30–50% SiO₂. Huang et al.¹⁵ compared the heat resistance, storage modulus, and glass-transition temperature (T_g) for a styrene-ethylene-butylene-styrene block copolymer (SEBS) and an aminofunctionalized SEBS hybrid containing SiO₂/TiO₂. They found that the heat resistance and storage modulus increased for the aminofunctionalized SEBS hybrid. However, a T_g decrease of 30°C was observed. Apparently, a functionalization of styrene might cause the domain morphology to vary somehow. Petrovi et al.¹⁶ also discussed the effect of the location of added nanosized SiO₂ on the physical and mechanical properties of a thermoplastic polyurethane/SiO₂ (TPU/SiO₂) hybrid. The T_g remained unchanged. The tensile strength and tear strength exhibited highest and lowest values, respectively. Zhang et al.¹⁷ carried out the synthesis and characterization of nanocomposites of silicon dioxide and PU and epoxy resin interpenetrating network. Nanocomposites with varying concentrations of nanosized SiO₂ particles were prepared by adding nanosilica to interpenetrating polymer networks of PU and epoxy resin. Their results showed that adding nanosized SiO₂ could improve the properties of compatibility, damping, and phase structure of interpenetrating polymer network matrices.

TABLE I
Preparation of TPU/SiO₂ Hybrids with HOAc as Catalyst at Room Temperature

Code	TPU	TS-5A	TS-10A	TS-15A	TS-20A
TPU (g)	20	20	20	20	20
THF (g)	180	180	180	180	180
TEOS (g)	0	3.65	7.72	12.25	17.36
HOAc (g)	0	8.41	17.79	28.22	40.00
THF (g)	0	3.65	7.72	12.25	17.36

TS-5A, TPU/SiO₂ hybrid containing theoretical 5 wt % SO₂ using HOAc catalyst; [TEOS]/[SiO₂] = 1 (mole ratio); [HOAc]/[TEOS] = 8 (mole ratio).

TABLE II
Preparation of TPU/SiO₂ Hybrids with Aqueous HCl as Catalyst at Room Temperature

Code	TPU	TS-5H	TS-10H	TS-15H	TS-20H
TPU (g)	20	20	20	20	20
THF (g)	180	180	180	180	180
TEOS (g)	0	3.65	7.72	12.25	17.36
H ₂ O (g)	0	1.26	2.67	4.23	6.0
HCl (g)	0	0.032	0.068	0.107	0.152
THF (g)	0	3.65	7.72	12.25	17.36

TS-5H, TPU SiO₂ hybrid containing theoretical 5 wt % SiO₂ using HCl as catalyst; [TEOS]/[SiO₂] = 1; (mole ratio); [H₂O]/[TEOS] = 4 (mole ratio); [HCl]/[TEOS] = 0.05 (mole ratio).

To the best of our knowledge, there is limited literature available on preparing TPE/SiO₂ hybrids using the sol-gel method, in particular, a TPU/SiO₂ hybrid. This work is undertaken to investigate the physical and thermal properties of this type of hybrid by employing different catalyst systems during sol-gel processing. Two types of catalyst systems, acetic acid (HOAc) and hydrochloric acid (HCl), were used to generate sol particles. The mixing of the sol solution and TPU solution to form a TPU/SiO₂ hybrid was carried out. Fourier transform IR (FTIR) spectra were recorded to depict the interfacial interactions. The mechanical properties such as the tensile strength were investigated at various concentrations of silica. Optical properties were evaluated to contrast the effect of the two catalyst systems. The fracture surface was revealed through scanning electron microscopy (SEM) to observe the degree of dispersion of SiO₂.

EXPERIMENTAL

Materials

The materials used in this study were TPU, tetraethoxysilane (TEOS), HCl, and HOAc. TPU was the ester type supplied by Bayer Taiwan Co. under the trade name KU2-8785. The hardness is Shore A 87, as provided by the supplier. TEOS was obtained from Acros. The catalysts were HCl and HOAc, which were reagent grade. All reagents and solvents were used as received.

Sample preparations

TPU was predried 2 h at 90°C in a dehumidified air-circulated oven prior to mixing. Various amounts of TEOS, tetrahydrofuran, deionized water, and catalysts (HCl or HOAc) based on Tables I and II were thoroughly mixed for 20 min under ambient conditions.^{18,19} Then, the above solution was added into a TPU solution followed by 20-min stirring to form a clear and homogeneous solution. The resulting solu-

tion was then transferred into a Teflon mold and air dried under ambient conditions for several days. A 0.7 mm thick sample was finally obtained after further drying to remove residual water and solvent at 30°C in a vacuum oven. Sample codes TS- x H in Table II or TS- x A in Table I denote x as the theoretical silica percentage in the hybrid and H and A as the HCl and HOAc catalyst systems, respectively.

Measurements

All test specimens were predried for 2 h at 90°C in a dehumidified air-circulated oven prior to analysis. The FTIR spectra were recorded on a spectrophotometer (Perkin-Elmer 1600) at a resolution of 4 cm^{-1} for 32 scans from 4000–600 cm^{-1} . The melting temperature (T_m) was measured using differential scanning calorimetry (Perkin-Elmer Pyris 1) at a heating rate of 20°C/min from 40 to 250°C. The T_g was determined via a dynamic mechanical analyzer (Perkin-Elmer Pyris 7e) under 3-point bending mode at a frequency of 1 Hz and a heating rate of 5°C/min from -70 to 50°C. Thermogravimetric analysis (TGA, Perkin-Elmer Pyris 6) was used to evaluate the thermal stability of the hybrid with a heating rate of 20°C/min under a nitrogen environment from 30 to 800°C. Tensile measurements were conducted at a crosshead speed of 200 mm/min using a Universal tensile testing machine (model GY6040A4). Sample dimensions were complied with the ISO 37 type III standard. The tensile strength and elongation were recorded. In addition, a cutting test was also employed to measure the fracture energy (G_c) using a razor blade at a cutting speed of 10 mm/min at around room temperature. The schematic sketch of the cutting test is shown in Figure 1. The pulling energy (P) and cutting energy (C) were calculated as follows^{20,21}:

$$P = 2f_A(1 - \cos\theta)/t \quad (1)$$

$$C = f/t \quad (2)$$

where f_A is the load, f is the cutting force, 2θ is the angle between two legs, and t is the cut thickness.

By measuring the cutting force and angle, the G_c was calculated from the sum of energies expended in both pulling and cutting, that is,

$$G_c = P + C \quad (3)$$

The optical properties were evaluated using a visible light spectrophotometer (Minolta, CM-3600D) at a scanning wavelength from 400 to 700 nm. The morphology of the fractured specimens was elucidated using a scanning electron microscope (JEOL 6335F-

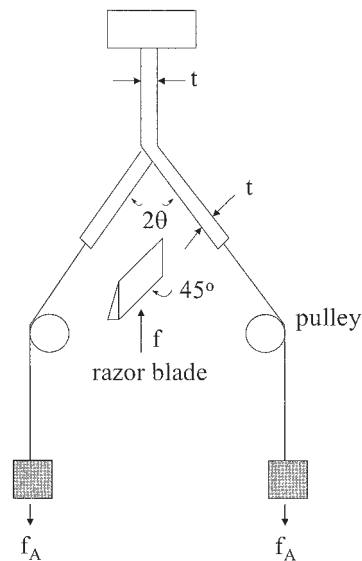


Figure 1 A schematic sketch of the cutting test.

SEM). All samples were sputtered with gold before further characterization.

RESULTS AND DISCUSSION

Structure and thermal characterization

Major regions of the FTIR spectra of the HCl and HOAc catalyzed TPU/silica hybrid are depicted in Figure 2 for a comparison, including the absorption regions of N—H (hydrogen bonded, 3331 cm^{-1}), C=O (free, 1725 cm^{-1} ; hydrogen bonded, 1702 cm^{-1}), and C—O (1164 and 1064 cm^{-1}).²² Basically, these results for pristine TPU indicate hydrogen bonding exists within the molecular chain. As silica was incorporated, most of the typical absorption bands remain unchanged. No new absorption band is observed. Further, the characteristic absorption band of Si—O specified at 1100 cm^{-1} is not seen and might be covered by C—O absorption regions. Yet, as silica concentrations increase, the absorption bands become broad. In general, the interaction of hydrogen bonding between the Si—O on silica and the functional groups on TPU might be overlapped in the N—H regions, so it is not clearly distinguishable on the TPU/silica hybrid. In addition, no catalyst systems effect is seen on the difference in the IR spectrum. Other characterizations such as a dynamic mechanical analyzer would be of help to provide a suggestive molecular interpretation on this hybrid and these will be discussed later.

To investigate the effect of the silica concentration on the thermal behavior of the hybrid, the T_g and T_m recorded from a dynamic mechanical analyzer and a differential scanning calorimeter were determined. Taking the HOAc catalyzed system as an example, the T_g slightly increases from -37 to -30°C (see Fig. 3),

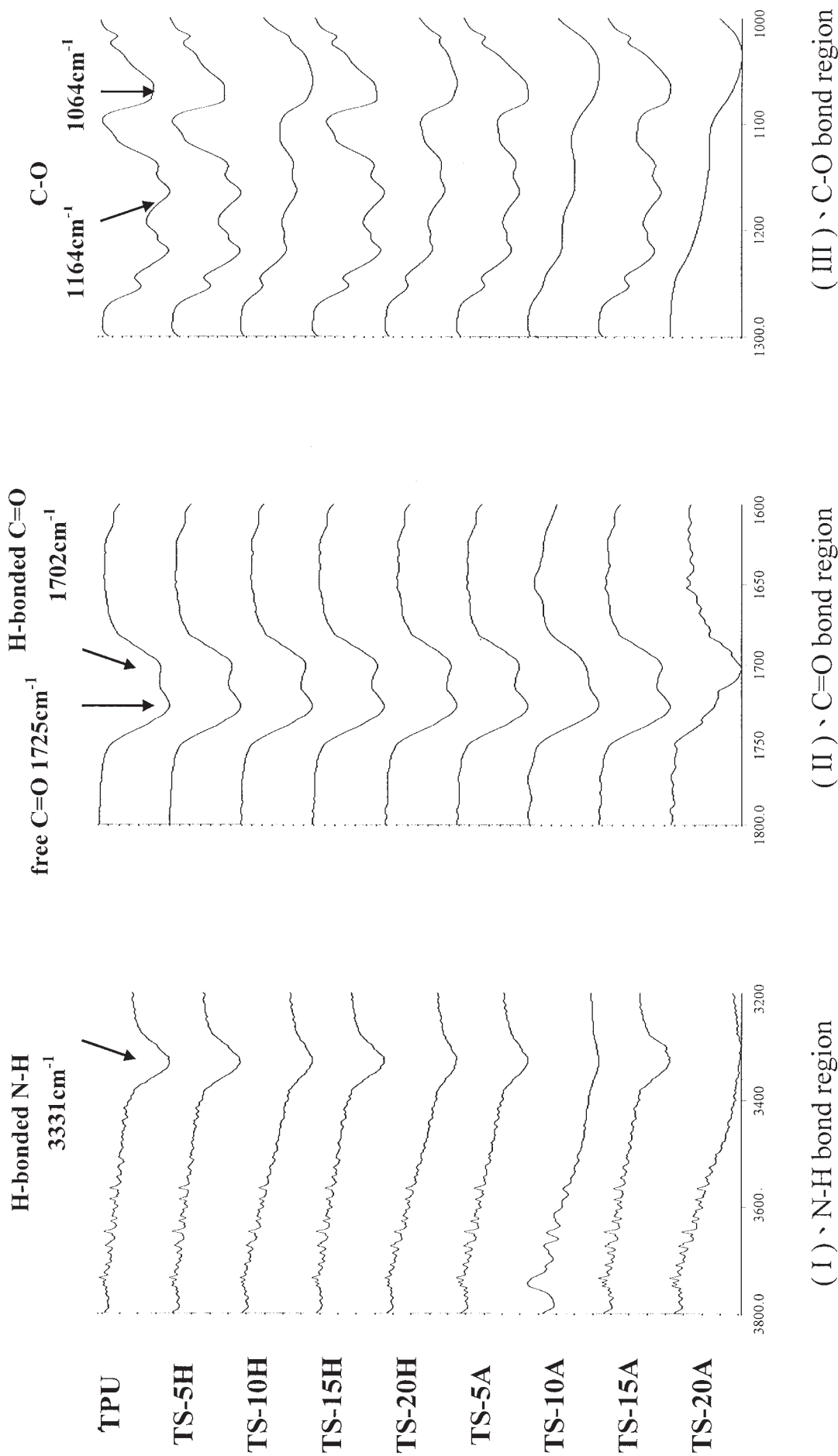


Figure 2 FTIR spectra of different functional groups of TPU/SiO₂ hybrids.

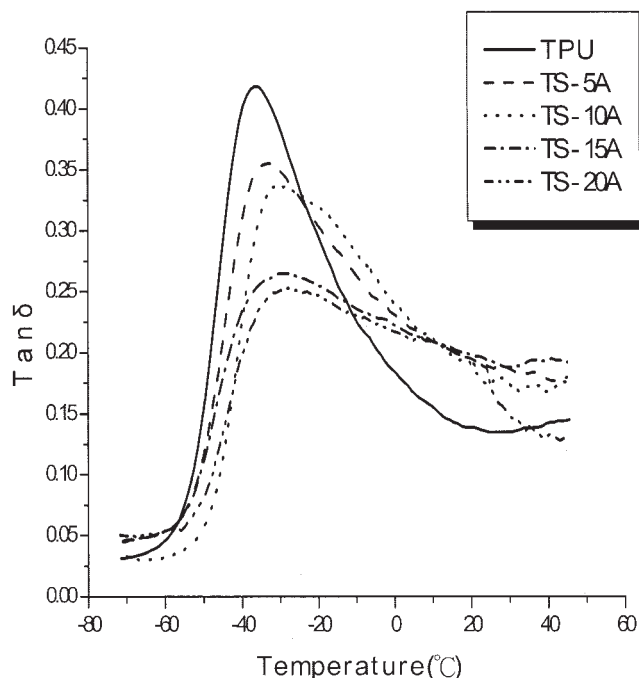


Figure 3 The variation of the loss tangent ($\tan \delta$) with various SiO_2 contents for TPU/ SiO_2 hybrids under the HOAc catalyst system.

which is due to a possible constraint stemming from a TPU/silica interaction. Moreover, the width of $\tan \delta$ tends to increase and the values of $\tan \delta$ become smaller, indicating an increase in the mutual interaction for the hybrid.²³ The storage modulus at -60°C for both catalyst systems is shown in Figure 4. As the silica concentration increases, the storage modulus increases correspondingly. The filler reinforcement remains valid at room temperature. This behavior indicates a certain interaction between the filler and TPU based on conventional fracture mechanics. As for the melting temperature, no notable differences are found in the effect of silica concentrations on the melting behavior perhaps because of the low crystalline TPU employed in this study. To evaluate the heating resistance of the hybrid, TGA was carried out and is illustrated in Figure 5. At a weight loss of 95%, the curve of pristine TPU crosses over those of hybrids at roughly 325°C . There is not much difference in the weight loss in this region. It seems the initial temperature of weight loss does not increase with increasing silica content. However, at a weight loss of 50%, silica tends to increase the thermal resistance of the hybrid. The ash contents measured at 600°C roughly correspond to theoretical amounts of silica from the sol-gel process. The results are shown in Table III. Similar findings are reached for the HCl catalyst system. In this study, theoretical amounts of silica are used for ease of comparison. Note that TPU is prone to hydrolysis at elevated temperature or for prolonged storage time at

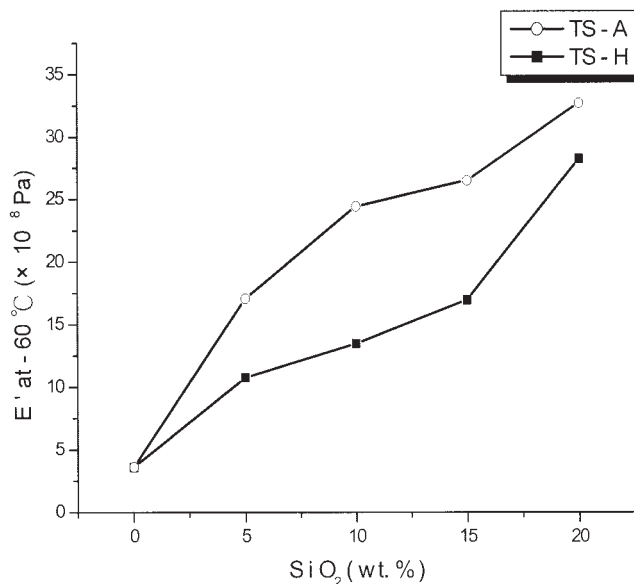


Figure 4 The variation of the storage modulus (E') with various SiO_2 contents for TPU/ SiO_2 hybrids under the HCl and HOAc catalyst systems at -60°C .

room temperature, yet the TGA results justify that this possibility is limited based on this sol-gel approach.

Mechanical properties

Figure 6 shows the effect of the theoretical SiO_2 content on the tensile strength of the hybrid under the

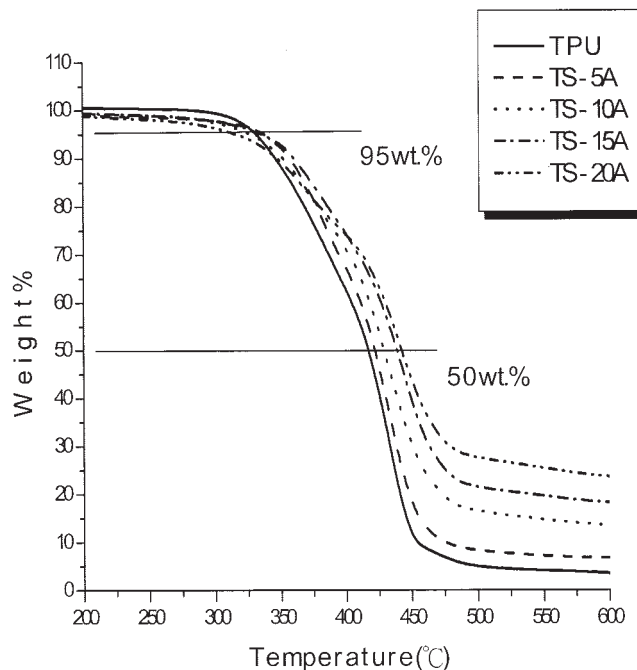


Figure 5 TGA curves of TPU/ SiO_2 hybrids with different SiO_2 contents and HOAc as the catalyst.

TABLE III
Actual Content of TPU/SiO₂ Hybrids Determined Through Thermogravimetric Analysis

Code	SiO ₂ actual content (wt %)	Code	SiO ₂ actual content (wt %)
TS-5H	5.8	TS-5A	5.4
TS-10H	11.3	TS-10A	12.0
TS-15H	15.5	TS-15A	15.7
TS-20H	18.8	TS-20A	21.1

HOAc and HCl catalyst systems. The difference in tensile strength is marginal for the two catalyst systems. A contrast of this is not intended because of a different recipe that is involved. Without a thorough investigation of the silica porosity and so forth, it is difficult to draw conclusions on the effect of the catalysts on the mechanical properties. However, because of the reinforcement of SiO₂, one still observes that the tensile strength is higher for the TPU/silica hybrid than pristine TPU at all dosages of silica under both catalyst systems. For the HOAc catalyst system, the maximum value reaches 49.8 ± 0.16 MPa at 15% silica. By contrast, for the HCl catalyst system, the maximum value is 49.3 ± 0.16 MPa at 10% silica. Those critical dosages of silica partly reflect the concentrations at which large agglomerates formed in the preparation of the hybrid, which is confirmed in the Optical Property and Morphology section later. This reinforcement effect might be explained using a conventional theory of fracture mechanism. For a conventional amorphous

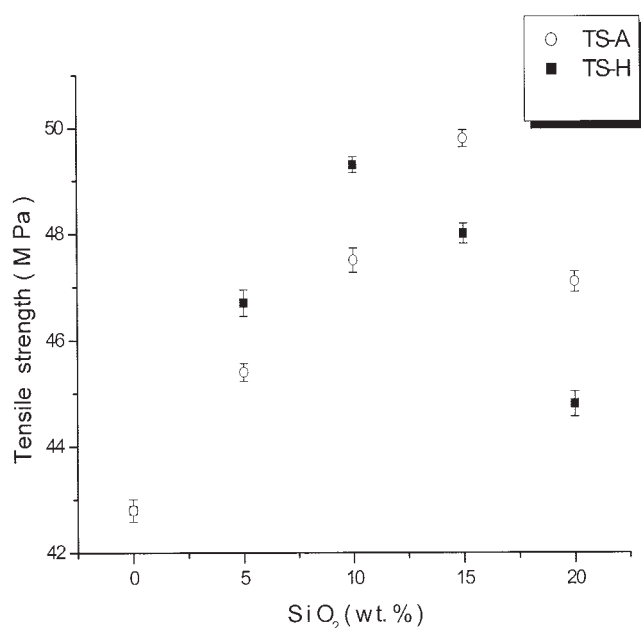


Figure 6 The effect of the SiO₂ content on the tensile strength of TPU/silica hybrids with HOAc and HCl as the catalysts.

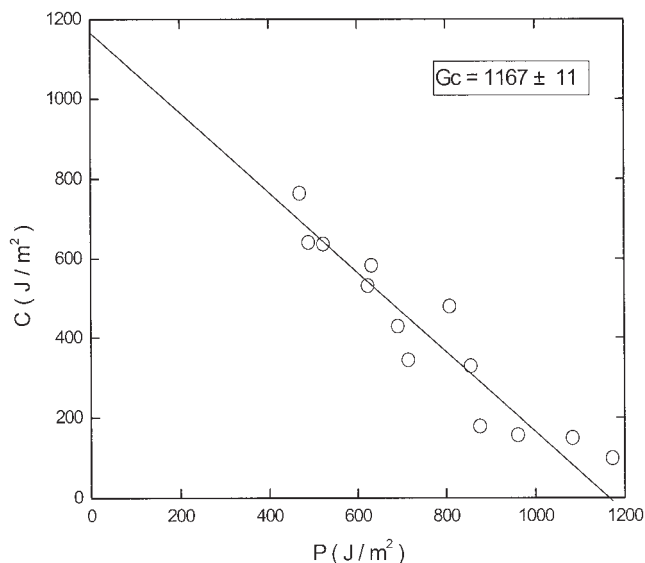


Figure 7 A plot of the cutting energy (C) versus the pulling energy (P) to determine the fracture energy (G_c) of TPU.

elastomer, the tensile strength would increase to some extent with increasing cure degree and decrease at very high degree of cure.²⁴ Here, because the TPU that is employed is a low crystalline polymer, one would expect similar results. One can treat SiO₂ as a physical crosslinker, and indeed a good interaction between TPU and silica was observed based on the previous characterization on the dynamic mechanical analyzer. This hypothesis seems to give a qualitative explanation for the observation of the mechanical properties.

To further understand the fracture behavior of the TPU/silica hybrid, one can confine the crack tip diameters on a nanoscale using a sharp razor blade. Cutting strength is evaluated by this recently developed method. A typical curve of cutting strength for pristine TPU is shown in Figure 7. A negative of slope of -1 is successfully drawn to obtain a cutting strength of 1167 ± 11 J/m², which indicates a good accordance of theory for this type of TPE. More measurements toward the comparison of the cutting strength were carried out to reduce the microyielding effect from segmented regions for TPU/silica under two types of catalysts. The results are depicted in Figure 8. Apparently, the cutting strength of TPU is about 20% larger than that of the TPU/silica hybrid at all silica concentrations. The lowest value attained is about 909 ± 10 J/m². Those values agree with other evaluations of the cutting strength for different types of materials, for instance, SB rubber,²¹ high-density polyethylene,²⁵ polypropylene/ethylene-propylene-diene monomer thermoplastic vulcanizate (TPV),²⁶ and SBS.²⁷ Higher cutting strength values for crystalline materials or block copolymers indicate that the microyielding effect still dominates the strength of the material even using a blade to reduce the zone of deformation. In

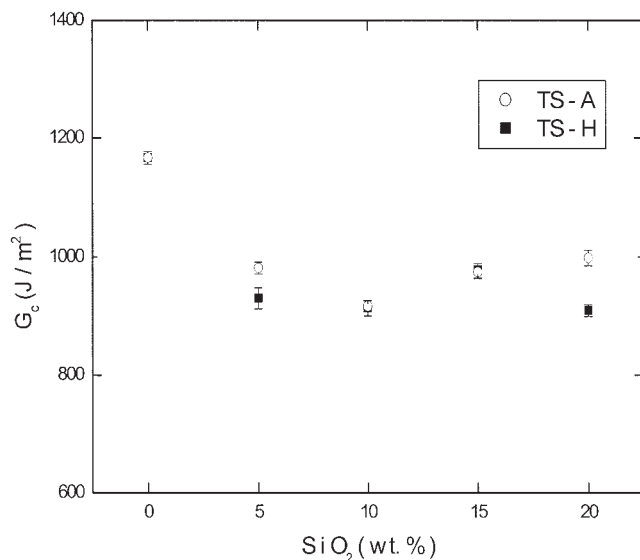


Figure 8 The effect of the SiO₂ content on the fracture energy (G_c) of TPU/SiO₂ hybrids with HOAc and HCl as the catalysts.

particular, the cutting strength seems to decrease and level off with increasing silica concentration. These results are unexpected but somewhat agree with our other study for carbon black filled elastomer via sulfur cure.²¹ A reduction of energy dissipation from silica crosslinking might account for this observation. In addition, the blade tip should be the same as the crack tip diameter on behalf of this cutting design; however, the crack tip diameter seems to change according to the previous manner. Accordingly, induced yielding from the blade is surmised and possible. It appears that filled hybrids show little or no reinforcement when the tear tip diameter is held constant. The phenomenon of reinforcement by fillers in the tensile test must be attributed to a filler-induced roughening of the tear tip.²⁸ Apparently, these values are a measure of the extent of plastic yielding around the tear tip, and good agreements are reached for this newly developed hybrid.

Based on the previous observations, one should be cautious on clarifying the role of reinforcement of silica in the hybrid. First, this reinforcement is clearly dependent on the deformation characteristics of the test. Second, would the aggregate of silica be required to promote tensile strength? Or would well-dispersed nanosilica in the hybrid be necessary to reinforce the elastomer? A recent work of Schaefer et al.²⁹ claimed a silica aggregate of a certain number of nanosilica particles was required to reinforce the SBR compound. Ikeda et al. also pointed out larger particles might entrap more molecular chains in the *in situ* silica during the sol-gel process, which rendered higher tensile strength for SBR.³⁰ Third, for this type of TPE hybrid, one might merely emphasize the formation of the

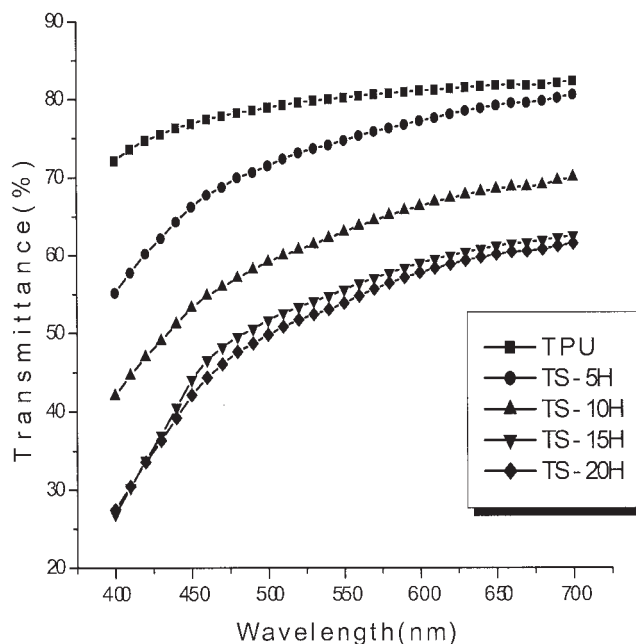


Figure 9 The transmittance of TPU/SiO₂ hybrids with different SiO₂ contents and HCl as the catalyst.

nanoparticle in the hybrid to improve many physical properties such as heat resistance, hardness, and mechanical properties. However, if silica disrupts the segmented domain of TPU, the mechanical properties might vary in light of several factors such as the crystalline domain, filler interaction, and so forth. Further study is needed to investigate these phenomena

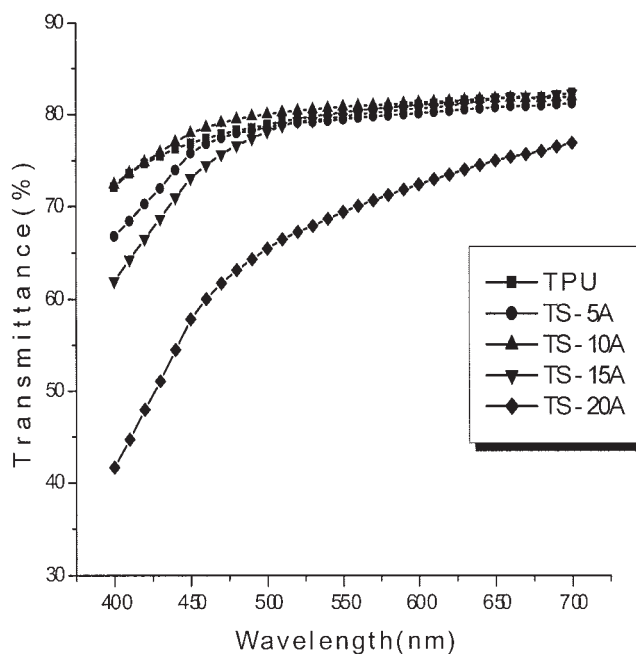


Figure 10 The transmittance of TPU/SiO₂ hybrids with different SiO₂ contents and HOAc as the catalyst.

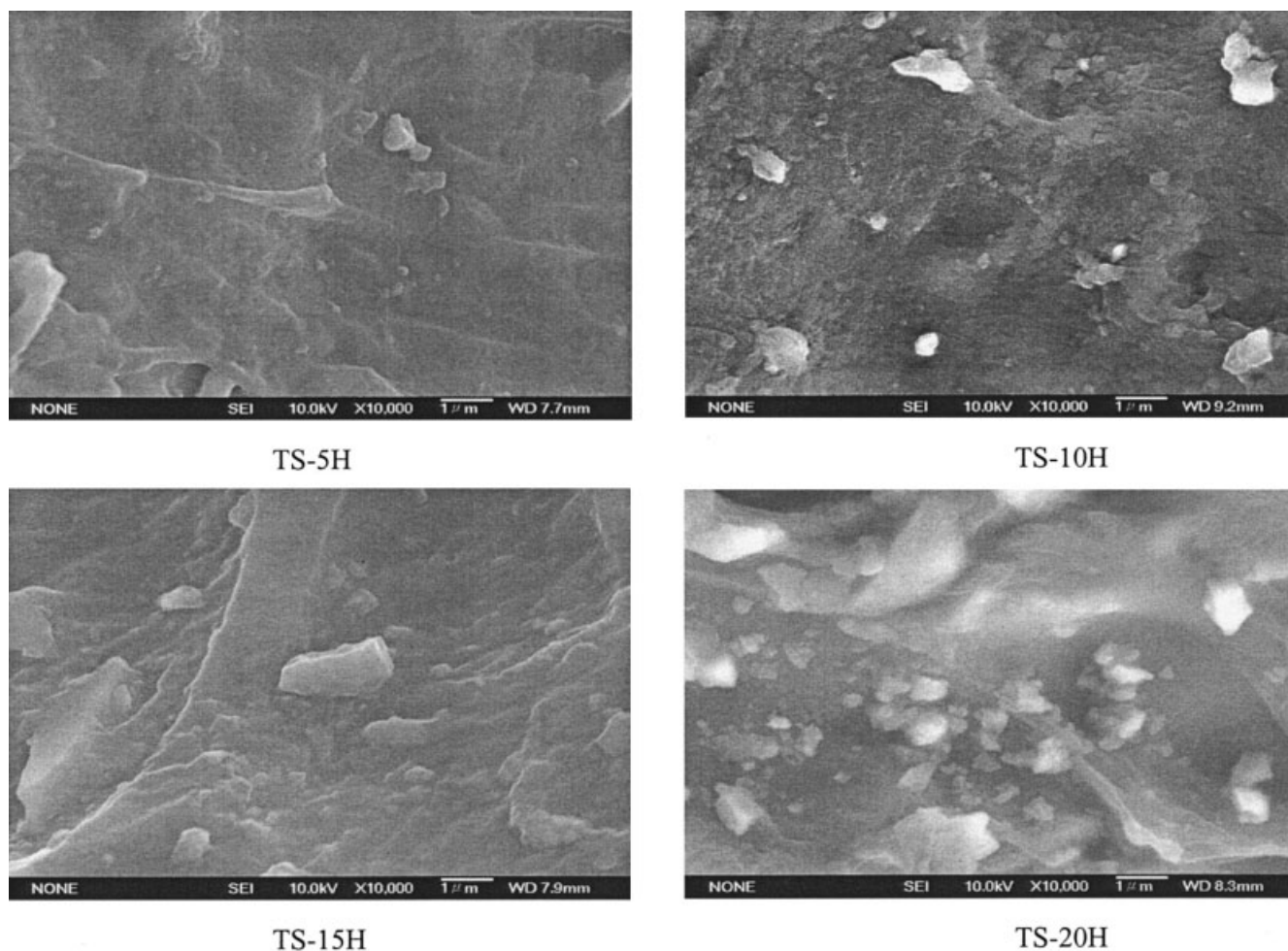


Figure 11 Scanning electron micrographs (original magnification $\times 10,000$) of the cross-section surface of hybrids with different SiO₂ contents and HCl as the catalyst.

in detail on the strength of the hybrid before reaching a conclusion.

Optical properties and morphology

Figure 9 shows the transmittance of TPU/silica hybrids with different SiO₂ contents using HCl as the catalyst. The transmittance progressively decreases with increasing SiO₂ content. Based on a visual comparison, the hybrid containing 5% SiO₂ remains transparent with pristine TPU. The hybrid containing 10% SiO₂ is somewhat translucent. Hybrids containing 15 and 20% SiO₂ are opaque. For a hybrid to remain transparent, SiO₂ should disperse in very fine scale to allow light to transmit easily. In a sense, only TS-5H seems to be classified as a nanocomposite. To further compare a hybrid prepared from the sol-gel process using HOAc as the catalyst, Figure 10 shows the transmittance of TPU/silica hybrids with different SiO₂ contents. The transmittance of the hybrids remains largely unchanged for TS-5A, TS-10A, and TS-15A

when compared with that of pristine TPU. In contrast, the transmittance of TS-20A decreases dramatically. Moreover, visual observation confirms that hybrids containing 5, 10, and 15% SiO₂ remain transparent as pristine TPU. Only the hybrid containing 20% SiO₂ gives a translucent image. Consequently, TS-5A, TS-10A, and TS-15A appear to form nanocomposites based on the current measurement. The results of a visual observation are generally consistent with optical measurements of the hybrids prepared under two catalyst systems. The major resulting difference in the optical properties from the two catalyst systems might be attributed to the water content in the recipe prescribed in Tables I and II. A certain amount of deionized water is required for the sol-gel process catalyzed by HCl. In fact, after the sol solution was mixed with the TPU solution, sol particles would tend to reside in the water medium. Because TPU is not compatible with water, the chance of forming an aggregate of *in situ* SiO₂ becomes higher instead of a fine dispersion in the TPU matrix, even though a certain interac-

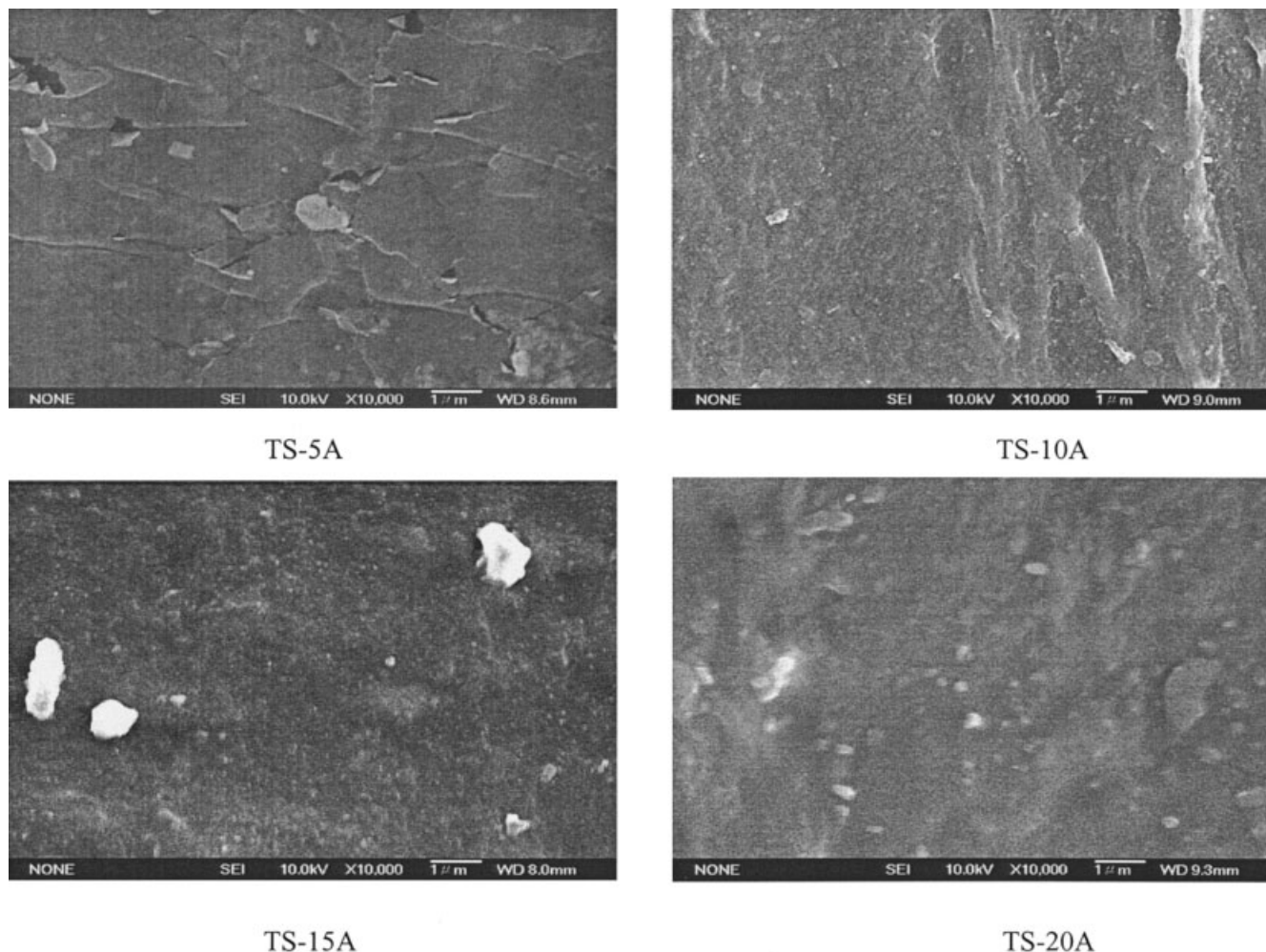


Figure 12 Scanning electron micrographs (original magnification $\times 10,000$) of the cross-section surface of hybrids with different SiO_2 contents and HOAc as the catalyst.

tion remains between TPU and SiO_2 . This situation becomes severe as the silica concentration increases. Accordingly, this competitive mechanism confers a different morphology for the resulting hybrid. In comparison, for the HOAc catalyzed system, minimal water, if any, is used, so the chance of obtaining well-dispersed *in situ* SiO_2 is higher unless a large amount of silica is formed in the sol-gel processing. The measurement of the optical properties confirms this finding.

To further confirm the aforementioned observations, SEM micrographs were taken for the fracture surfaces of the hybrids. The results for the HCl catalyzed system are depicted in Figure 11. For the TS-5H hybrid, nanoparticles are well dispersed in the TPU matrix, which indicates the formation of a nanocomposite in some way. As the concentrations of *in situ* SiO_2 increase, aggregations on the order of microns are observed. This feature agrees with the previous measurement on the optical property and a visual observation of the hybrid. The results for the HOAc catalyzed system are shown in Figure 12. The distinct morphology of the fracture surface of HOAc

catalyzed hybrids indicates well-mixed SiO_2 particles in the TPU matrix for TS-5A, TS-10A, and TS-15A. Although in some cases large particles are still seen for TS-15A, the hybrid remains transparent based on the previous measurement. Generally, the average particle sizes in HOAc are smaller than those in the HCl catalyzed system based on these micrographs. Recall that the tensile strength drops at a higher loading of *in situ* SiO_2 , so these SEM observations provide a possible explanation for the decrement of the mechanical property. It is probable that the aggregation of SiO_2 might increase the flaw size of the hybrid, a prime factor of determining the tensile strength of materials. However, the tensile strength is still higher than that of pristine TPU, indicating a certain interaction remains between the TPU and SiO_2 of the hybrid prepared through this sol-gel process.

CONCLUSIONS

A TPU/ SiO_2 hybrid was prepared using the sol-gel process. Two types of catalyst systems including

HOAc and HCl were used to generate sol particles. The mixing of the sol solution and TPU solution was carried out to form the TPU/SiO₂ hybrids. The FTIR spectra and dynamical mechanical properties were recorded to depict the enhanced interfacial interaction. The actual silica content determined from TGA roughly corresponds to the *in situ* theoretical silica content. The mechanical properties such as the tensile strength and cutting strength were investigated at various concentrations of *in situ* silica. The tensile strength increased at all concentrations of silica. In contrast, the cutting strength decreased, probably because of a reduction of the energy dissipation from silica as chemical crosslinks. Measurements of the mechanical properties should be carried out according to deformation characteristics and should not rely on only one test. The HOAc catalyzed system showed better optical properties than the HCl catalyzed system, perhaps because of a difference in the water content in the prescribed recipe. Nanocomposites appeared to form at low dosages of *in situ* silica concentrations. The fracture surface was revealed through SEM to observe the degree of dispersion of SiO₂, which in turn confirmed the results for the optical and mechanical properties.

Financial supports from Plastics Industry Development Center are greatly appreciated.

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