Mechanical Characterization of Polyhedral Oligomeric Silsesquioxane/Polypropylene Blends

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ABSTRACT: Polypropylene blends with polyhedral oligomeric silsesquioxanes (POSS) bearing different alkyl groups were investigated to elucidate the effect of the alkyl group length on the mechanical behavior of the blends. In particular, blends of polypropylene (PP) with either octamethyl-POSS, octaisobutyl-POSS, or isooctyl-POSS were studied. Differential scanning calorimetry evidenced only minor changes in the degree of crystallinity compared to neat PP. Uniaxial tensile tests showed that the incorporation of octamethyl-POSS induces an increase in Young's modulus and a reduction of the yield strength in comparison with unfilled PP. By contrast, upon the incorporation of octaisobutyl-POSS and isooctyl-POSS, both Young's modulus and the yield strength were found to decrease by increasing the POSS content. It is suggested that POSS behave as particles having a siliceous hard-core surrounded by a hydrocarbon soft-shell, which limits the stress transfer from the matrix to the core in dependence on the length of the alkyl groups. Finally, the essential work of fracture method was employed to study the fracture behavior of octamethyl-POSS/PP blends, with different POSS contents (0, 3, and 10 wt %). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 935–943, 2007

Key words: differential scanning calorimetry; fracture; mechanical properties; nanocomposites; poly(propylene)

INTRODUCTION

Polyhedral oligomeric silsequioxanes (POSS) are hybrid nanoparticles (dimension ∼1.5 nm) consisting of an inorganic cage $(SiO_{1.5})_n$ ($n = 6, 8, 10\ldots$) to which n organic substituents are linked (see Fig. 1).[1] A variety of reactive and nonreactive functional groups can be introduced into their molecule so that the POSS chemistry is very flexible. POSS functionality is largely exploited to incorporate these nanofillers into polymer matrices by copolymerization or chemical grafting. POSS have been covalently bound to several polymers such as poly(methyl methacrylate),[2] polystyrene,[3] polyethylene,[4] polyamide 6 (Ref. 5), and epoxies.[6] In many cases, the resulting nanocomposites have shown enhanced properties such as increased thermal stability, higher glass transition temperature (T_g), better flame resistance, and improved mechanical stiffness in comparison with the corresponding neat polymers.

While the number of publications on POSS-copolymers has steeply increased in the past few years, up-to-date only limited attention has been paid to systems in which POSS are physically blended with polymers. Fu et al.[7] analyzed the rheological behavior of ethylene-propylene copolymer melts containing POSS molecules. They found that octamethyl-POSS formed crystal aggregates, which caused physical gelation in the melt state. In addition, these nanocomposites had higher T_g and increased storage modulus than neat polymer. In contrast, Kopesky et al.,[8] who investigated blends of poly(methyl methacrylate) with acrylic-POSS, observed that the incorporation of POSS caused a reduction in T_g and a decrease in the storage modulus. A few papers have appeared in which the properties of POSS copolymers have been compared with those of the corresponding blends.[9–13] In general, when POSS are physically blended, poorer properties and a higher tendency towards phase separation are observed than when they are chemically bonded to polymer chains. Nevertheless, improved thermomechanical behavior in comparison with the corresponding neat polymers has been reported for some blend systems.[7,11] Thus melt blending, which looks attractive owing to its easy industrial implementation, represents a possible route for obtaining POSS-based nanocomposites with valuable properties. On the other hand, the variability in performance exhibited by these blends makes evident that reliable

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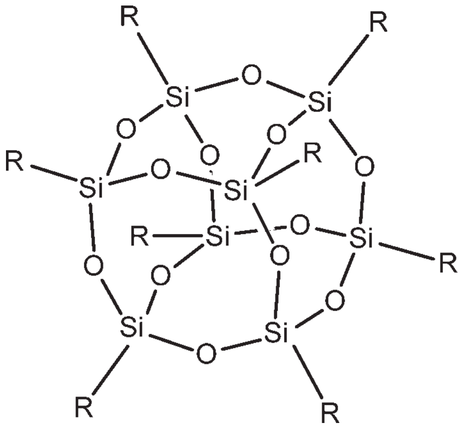

Figure 1 Structure of a POSS molecule bearing eight nonreactive groups (R).

structure-property relationships are still lacking for such systems. In particular, proper criteria for the selection of the POSS organic groups, which determine both POSS miscibility and matrix-filler interface and ultimately the properties of the composite materials, are yet to be established.

In this work, the influence exerted by the length of POSS alkyl chain on the mechanical behavior of POSS/polypropylene blends was investigated. To this purpose, mixtures of polypropylene (PP) with three types of POSS, namely octamethyl-POSS, octaisobutyl-POSS, and isooctyl-POSS were studied. The preparation, morphological characterization, and thermal stability of these materials were previously reported.[14] Here their mechanical behavior was investigated by uniaxial tensile tests and their thermal properties by differential scanning calorimetry (DSC). Our results indicate that mechanical stiffness and strength decrease with increasing length of the hydrocarbon residues. Reinforcement with respect to neat PP was observed only with octamethyl-POSS. For this system, preliminary investigations on the fracture behavior were also carried out using the essential work of fracture (EWF) approach.

EXPERIMENTAL

Materials

A summary of the materials investigated, which differ either in the POSS type or content, is reported in Table I. The various POSS/PP blends were prepared via melt blending in a Brabender mixer as previously reported.[14] The corresponding unfilled PP was similarly processed in Brabender to ensure a thermomechanical history analogous with those of the blends. All the materials were compression-molded to produce plaques, 0.5 mm thick, suitable for the preparation of the specimens for the mechanical tests. The systems containing either octamethyl-POSS or isooctyl-POSS, and the corresponding neat polymers, were compression-molded at 190°C, whereas the materials containing octaisobutyl-POSS, and the corresponding neat polymer, were molded at 230°C.

TABLE I
Composition of the Materials Investigated

Materials	POSS content (wt %)	Inorganic content (wt %)
PP/octamethyl-POSS	0	0
	3	2.3
	10	7.8
PP/octaisobutyl-POSS	0	0
	3	1.4
	6	2.8
	10	4.8
PP/isooctyl-POSS	0	0
	3	0.9
	10	3.1

Thermal characterization

Thermal analysis was performed on a Q100 TA Instruments DSC by heating samples of about 9 mg, obtained from the compression molded plaques, from −90 to 200°C under nitrogen flow and at a scanning rate of 10°C/min. The crystallinity degree of PP was evaluated through the following relationship:

$$X_c = \frac{\Delta H_f}{(1-f)\Delta H_f^0} \quad (1)$$

where ΔH_f and ΔH_f^0 are the enthalpy of fusion of the polymer in the blend and in 100% crystalline PP, respectively, while f represents the weight fraction of POSS in the blend. In our calculations we assumed that ΔH_f^0 is 209 J/g.[15]

Mechanical characterization

Tensile tests were carried out by an Instron dynamometer (model 3366) on specimens prepared by cutting rectangular coupons with length of 90 mm and width of 7 mm from the compression molded plaques of the various materials. All the tests were performed using a distance between the grips of 60 mm, at room temperature and a crosshead speed of 2 mm/min. All the properties examined were evaluated on an average of at least 5 specimens.

The study of the low rate fracture behavior of octamethyl-POSS/PP blends and the corresponding neat polymer was performed by applying the method of the plane-stress EWF, following a multi-specimen technique.[16,17] The small thickness of the compression molded plaques obliged the authors to choose a plane-stress fracture mechanics approach. For each material, a series of sharply notched single edge notched in tension (SEN(T)) specimens, with length $L = 70$ mm, width $W = 10$ mm, and nominal ligament length ranging between 2 and 7 mm, was prepared from the compression molded plaques. Each specimen was tested to complete failure by means of the dynamometer with distance between the grips $H_0 = 30$ mm, using a crosshead speed of 1 mm/min at room temperature. The real ligament length (l) of each specimen was measured on the fractured specimen using an optical traveling microscope. For each material examined, five ligament lengths were investigated. This small number is due to the limited amount of material available for the preparation of the specimens. Though the EWF test protocol proposed by ESIS (Technical Committee 4; Plastics, Adhesives and Composites)[18] requires that a minimum of 25 specimens per material should be tested, in this work, the EWF approach was tentatively applied.

RESULTS AND DISCUSSION

Thermal analysis

DSC analyses were carried out on samples taken from the compression molded plaques, without previous heat treatments, to establish evidence of possible relationships between the degree of crystallinity of the matrix and the mechanical behavior of the blends. The results reported in Table II evince that the incorporation of POSS particles induces only a slight decrease in the degree of crystallinity for octaisobutyl- and isooctyl-POSS/PP blends, whereas it leaves the crystallinity practically unmodified in octamethyl-POSS/PP blends, with respect to the corresponding neat PP.

Tensile stress-strain behavior

Typical stress-strain curves of the various materials investigated are reported in Figure 2. From the experimental stress-strain curves, data of elastic modulus (E) and tensile strength (σ_y) were obtained. The results are summarized in Table III.

It can be clearly observed that the presence of POSS particles modifies the material stress-strain behavior, with respect to the corresponding neat PP, with dependence on the POSS type dispersed in the polymer matrix.

The effects promoted by the incorporation of POSS particles on the material stiffness are shown in Figure 3, where the ratio between the elastic modulus of the blends and that of the corresponding neat polymer is shown. It turns out that, at 10 wt % POSS content, in the blend containing octamethyl-POSS, the addition of POSS particles determines an increase in the material stiffness, whereas for the corresponding blends with either octaisobutyl- or isooctyl-POSS, no increase in stiffness is observed. The Young's modulus is either unmodified (octaisobutyl-POSS) or even decreased (isooctyl-POSS) with respect to the corresponding neat PP. From Figure 3, it emerges also that for the blends containing either octamethyl- or isooctyl-POSS, the material stiffness varies monotonically with increasing POSS content, whereas for octaisobutyl-POSS systems a minimum is observed at about 3 wt % POSS content. Further, our results show that the incorporation of POSS molecules within PP matrix modifies the yielding behavior of the material, determining a decrease in the material strength that depends on the type of POSS molecules dispersed within the polymer (see Table III). With respect to the corresponding neat polymer, the addition of 10 wt % POSS to PP causes a yield stress reduction of about 14% for both octamethyl- and octaisobutyl-POSS/PP blends, whereas a more pronounced abatement (24%) is observed for the isooctyl-POSS/PP blend. Further, from Figure 2 it is also clear that, for each POSS/PP series, the presence of POSS particles within PP induces a decrease in the elongation at break with respect to neat polymer.

The lack of stiffness enhancement observed in POSS/PP blends containing either octaisobutyl- or isooctyl-POSS with respect to the corresponding neat polymer is clearly in contrast with the behavior of particulate composites containing rigid fillers that

TABLE II
Thermal Properties of POSS/PP Blends and Neat Polymers

	Octamethyl-POSS/PP		Octaisobutyl-POSS/PP		Isooctyl-POSS/PP	
POSS content (wt %)	T_m (°C)[a]	X_c (%)[b]	T_m (°C)[a]	X_c (%)[b]	T_m (°C)[a]	X_c (%)[b]
0	165.9	42	161.8	46	164.1	45
3	165.8	43	164.7	44	165.6	43
6	–	–	163.6	44	–	–
10	165.4	42	163.1	43	164.6	43

[a] Melting temperature of the PP crystalline phase (peak temperature).
[b] Degree of crystallinity of the PP phase, evaluated according to eq. (1).

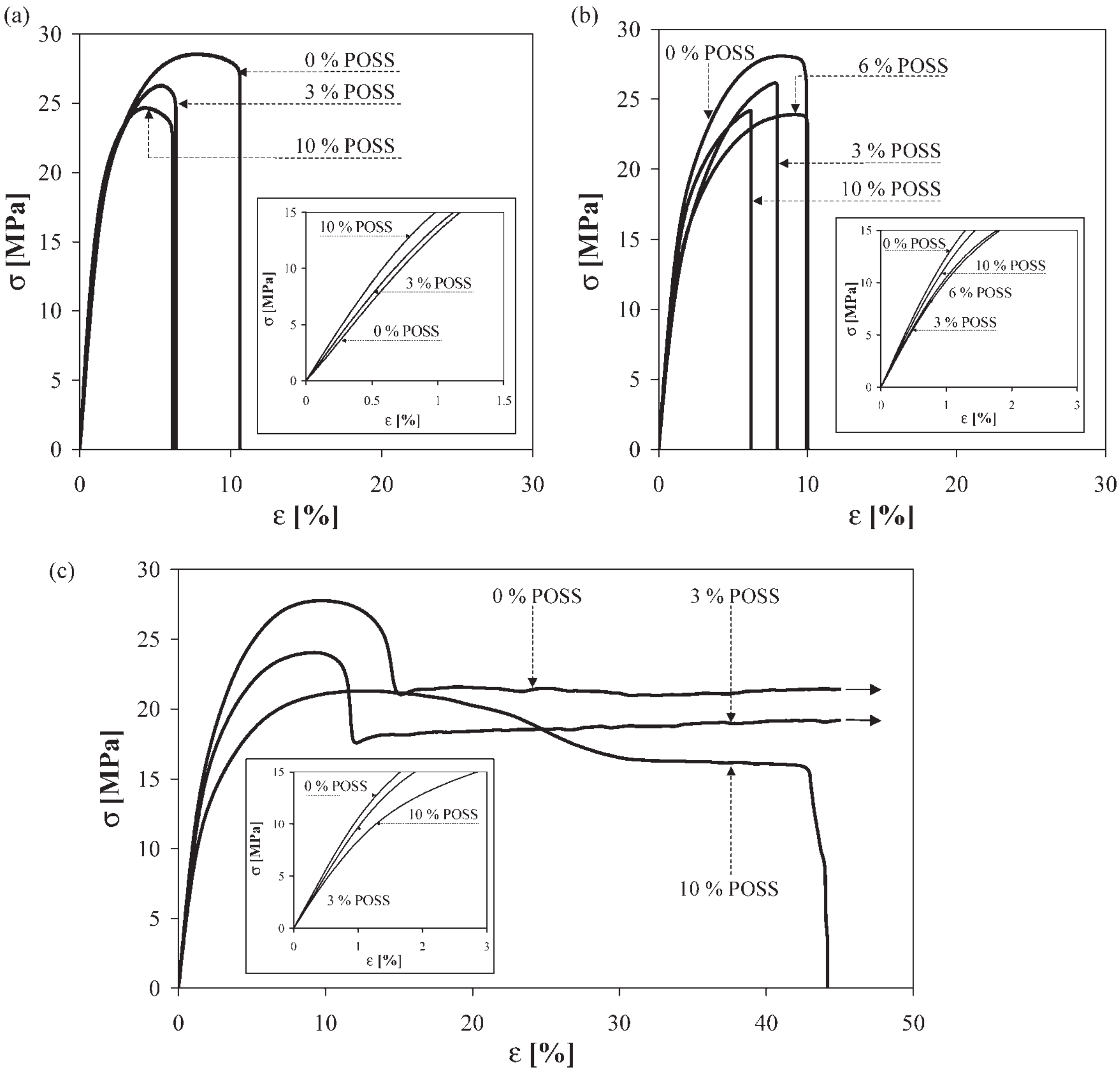

Figure 2 Typical stress-strain curves of the PP-based blends containing either (a) octamethyl-POSS, or (b) octaisobutyl-POSS, or (c) isooctyl-POSS as dispersed phase; % stands for wt %.

usually exhibit reinforcement effects. These results can be only partially ascribed to the very limited decrease in the degree of crystallinity of the matrix with respect to neat PP, which was evidenced by DSC analyses. Rather, they can be tentatively explained by considering the role played by the organic groups (R in Fig. 1) of POSS molecule. The organic substituents employed in this work were hydrocarbon chains of different length, constituted either by one (octamethyl-POSS), four (octaisobutyl-POSS), or eight (isooctyl-POSS) carbon atoms. Thus these POSS molecules can be considered as particles having an identical siliceous hard-core enveloped by a hydrocarbon soft-shell of variable thickness, being octamethyl-POSS and isooctyl-POSS the particles with the thinnest and the thickest soft-shell, respectively.

In composites where a polymer matrix embeds particles having a hard-core surrounded by a soft-shell, the stress transfer from the matrix to the core, which is the part of the particle directly responsible for the reinforcement, can be considerably impaired and, as a consequence, the reinforcing action could be even nullified. It has been shown by Riccò et al.,[19] by means of a micro-mechanical analysis of an elementary, single particle model, that, in case of a hard-core/soft-shell particle embedded in a polymer matrix, the stiff core does not share the load if the thickness of the shell is higher than about 25% of the radius of the hard core. This indicates that the thickness of the shell, with respect to the dimension of the core, is a key factor in permitting the rigid part of the particle to express a reinforcing effect.

The different effects induced by POSS particles on the mechanical stiffness in octamethyl- and isooctyl-POSS/PP systems at 10 wt % POSS content can be therefore explained by considering that, in the latter, the presence of a thick soft-shell practically hinders

TABLE III
Tensile Properties of the Various Materials

	Octamethyl-POSS/PP		Octaisobutyl-POSS/PP		Isooctyl-POSS/PP	
POSS content (wt %)	E (MPa)	σ_y (MPa)	E (MPa)	σ_y[a] (MPa)	E (MPa)	σ_y (MPa)
0	1450 ± 57	29 ± 0.8	1280 ± 34	28 ± 0.5	1100 ± 96	28 ± 0.3
3	1480 ± 58	27 ± 1.2	1010 ± 32	25 ± 1.1	980 ± 27	24 ± 1.3
6	–	–	1070 ± 38	23 ± 0.4	–	–
10	1630 ± 43	24.6 ± 0.22	1270 ± 75	24[b]	820 ± 16	21.4 ± 0.17

[a] Taken as the stress at 6% strain.
[b] Average of only two data.

stress transfer from the polymer matrix to the inorganic hard-core of the POSS particle. In the system containing octamethyl-POSS, instead, the soft-shell is thin enough to make the inorganic part of the POSS share the load, thus manifesting a reinforcement action. Moreover, it must be taken into account that, since in a composite characterized by a specific POSS content, the longer the lateral organic substituent the lower the amount of inorganic material that might exhibit reinforcement action, the amount of inorganic material dispersed in a isooctyl-POSS/PP composite is much lower than that dispersed in a system containing octamethyl-POSS with the same POSS content (see Table I).

Morphological analyses carried out on these systems showed a clear evidence for phase separation and the formation of POSS aggregates.[14] It is reasonable to suppose that such aggregates are constituted by rigid inclusions (POSS hard-cores) embedded in a soft matrix (POSS organic groups), whose volume fraction within the aggregate depends on the bulkiness of the lateral substituents. Therefore it can be expected that isooctyl-POSS aggregates behave as soft, rubber-like particles, which induce a stiffness reduction, while aggregates of octamethyl-POSS act as stiff fillers and thus are able to supply mechanical reinforcement.

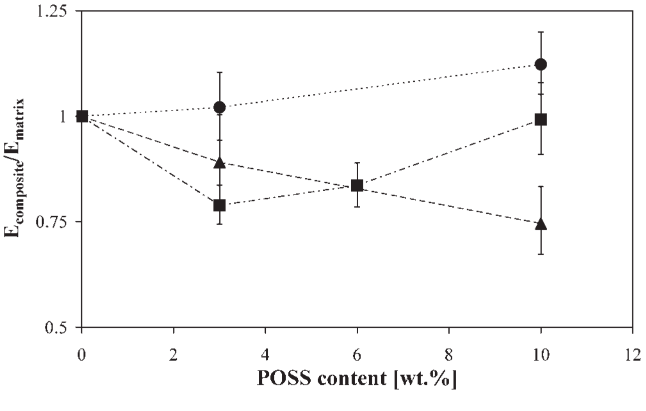

Figure 3 Young's modulus of the various POSS/PP blends, normalized on the modulus of the corresponding unfilled polymer, as a function of POSS content; symbols: (●), octamethyl-POSS/PP; (■), octaisobutyl-POSS/PP; (▲), isooctyl-POSS/PP.

The above hypotheses were tentatively verified by comparing the experimental results obtained for isooctyl-POSS/PP systems with data calculated by the application of the analytical micro-mechanical model proposed by Kerner,[20] which permits calculation of the elastic modulus of a polymer composite containing nearly spherical particles with elastic modulus much lower than polymer matrix. For rubber-filled polymers or foams, the Kerner equation is:

$$\frac{1}{G_c}=\frac{1}{G_1}\left[1+\frac{15(1-\upsilon_1)}{7-5\upsilon_1}\cdot\frac{\Phi_2}{\Phi_1}\right] \qquad (2)$$

where G_c and G_1 are the shear modulus of the composite and the matrix, respectively, υ_1 the Poisson's ratio of the matrix, Φ_2 and Φ_1, the volume fraction of filler and matrix, respectively. From the experimental value of Young's modulus of the neat PP used as matrix for isooctyl-POSS/PP systems, by the application of eq. (2), Young's modulus of a theoretical rubber-filled PP having the same continuous phase as isooctyl-POSS/PP systems can be determined assuming the same Poisson's ratio of 0.33 for PP and for the blends. In Figure 4 the decrease in the experimental elastic modulus, with respect to the neat polymer, induced by the presence of isooctyl-POSS in the POSS/PP systems is compared with that theoretically predicted as promoted by the presence of rubber particles or holes. In the Figure, the experimental values are plotted taking into account that density values of 0.9 and 1.1 g/cm^3 were used for PP and isooctyl-POSS, respectively, to convert weight fractions to volume fractions.[21] A fair agreement between the experimental data and the results from the model can be observed.

Young's modulus of octaisobutyl-POSS/PP materials does not decrease monotonically with the POSS concentration but presents a minimum at 3 wt % POSS content. While a modulus reduction of 21% compared to neat PP is observed in the blend with 3 wt % POSS, the system with 10 wt % POSS has nearly the same stiffness as unfilled PP. The increase in modulus observed at POSS contents greater than

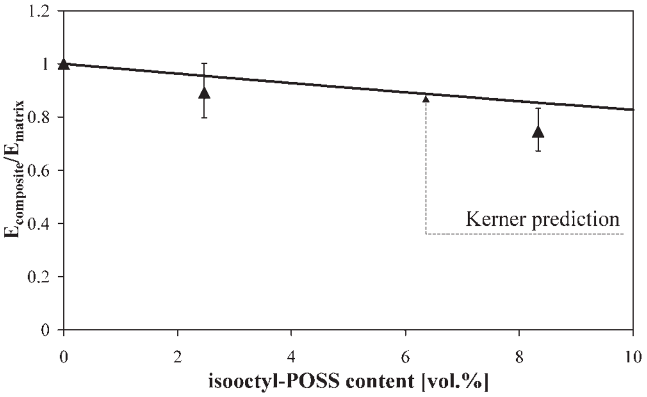

Figure 4 Young's modulus of the isooctyl-POSS/PP blends, normalized on the modulus of the corresponding unfilled polymer, as a function of the POSS phase volume fraction; the experimental results are compared with data predicted via eq. (2) (see text).

3 wt % could be related to the occurrence of changes in the material morphology, which would contrast the weakening effect of the POSS soft-shell. In fact, while at 3 wt % isolated, almost equiaxic, POSS crystals were observed; at 10 wt %, a fraction of POSS aggregates were arranged along preferential orientations and formed ribbon-like structures.[14] Furthermore, in the blend with 10 wt % of octaisobutyl-POSS, X-ray diffraction analysis provided evidence of the presence of β and γ PP crystalline phases, besides the α-form, which was the only crystalline phase observed in the other materials investigated. It is worth noting that, while the β-phase has higher tensile strength and slightly reduced stiffness in comparison with the α-form,[22] the occurrence of γ-phase in PP has been associated with molecular orientation and enhanced Young's modulus and tensile strength.[23]

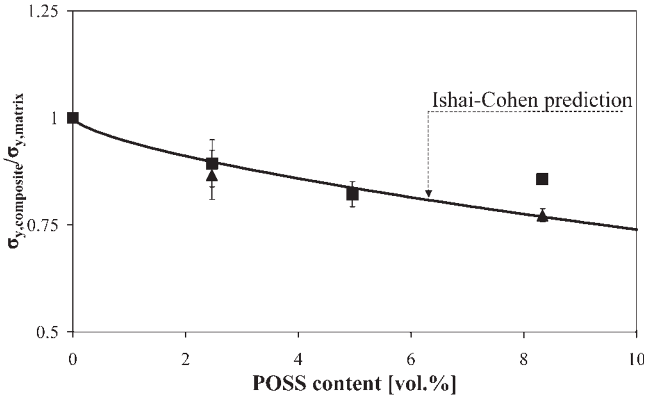

Figure 5 Tensile yield stress of the isooctyl-POSS/PP and octaisobutyl-POSS/PP blends, normalized on the yield stress of the corresponding unfilled polymer, as a function of the POSS phase volume fraction; the experimental results are compared with data predicted via eq. (3) (see text); symbols: (■), octaisobutyl-POSS/PP; (▲), isooctyl-POSS/PP.

As anticipated, the presence of POSS particles in the octamethyl-, octaisobutyl-, and isooctyl-POSS/PP blends promotes a decrease in the material mechanical strength, with respect to the corresponding neat PP. For the systems containing either octaisobutyl- or isooctyl-POSS particles, this result could again be explained by the core/shell nature of the POSS molecules. POSS particles can be supposed to have quite the same effect as voids on the stress distribution in the surrounding matrix under conditions of tensile loading. This can be tentatively verified by comparing the experimental results obtained for such systems with data calculated by the application of the effective area model proposed by Ishai and Cohen.[24] The effective area model, successfully used by various authors,[25–27] is an analytical model that predicts the yield stress in polymer-based composites containing either rigid spherical particles unbonded to the matrix or voids, and that is typically extended also to rubber-filled polymers. According to this model:

$$\sigma_{yc} = \sigma_{y1}(1 - 1.21\,\Phi_2{}^{2/3}) \qquad (3)$$

where σ_{yc} and σ_{y1} are the yield stress of the composite and matrix, respectively, and Φ_2 the volume fraction of the secondary phase. From the experimental value of the tensile yield stress of the neat PP used as matrix, by the application of eq. (3), the yield stress of a PP-based system containing uniformly dispersed holes can be determined. In Figure 5 the decrease in tensile yield stress induced by the presence of either octaisobutyl-POSS or isooctyl-POSS, with respect to the corresponding neat polymer, is compared with that theoretically predicted as promoted by the presence of holes. For PP and POSS molecules the same density values, as used in the application of the Kerner model [see eq. (2)], were employed to convert the weight fractions to the volume fractions. Good agreement between the experimental data and the results predicted by the model is observed for both families of blends, with the exception of the octaisobutyl-POSS/PP system containing 10 wt % POSS, whose strength is higher than that predicted by eq. (3). As for the Young's modulus, this disagreement might be ascribed to morphological modifications occurring in the presence of high octaisobutyl-POSS contents.

It has been verified that the decrease in the yield stress induced by POSS particles in the octamethyl-POSS/PP blends, with respect to the corresponding neat PP, does not conform to the predictions of Ishai-Cohen model, consistently with the fact that the model was developed for polymer composites containing voids, rubbery particles, or rigid particles completely unbonded.

A deeper analysis of the deformation mechanisms at the basis of the yielding behavior of the various

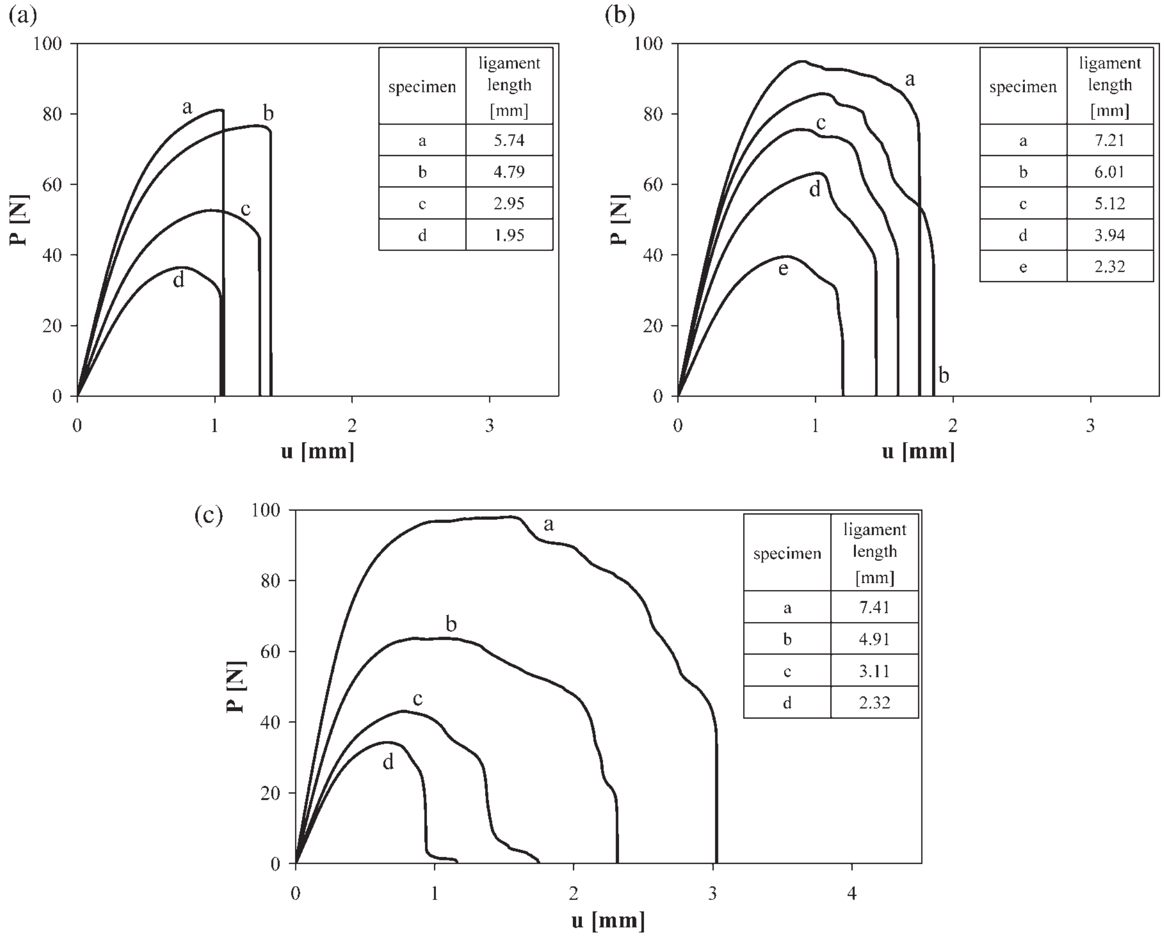

Figure 6 Load (P) versus displacement (u) curves produced in EWF tests carried out on SEN(T) specimens with various ligament lengths for: (a) neat PP, (b) octamethyl-POSS/PP blend with 3 wt % of POSS, (c) octamethyl-POSS/PP blend with 10 wt % of POSS.

POSS/PP systems, and the corresponding neat polymers, would require a larger material amount; this could be the matter of further studies.

Fracture behavior

In EWF testing, to evaluate the specific essential work of fracture of a material, the total energy to fracture W_f, calculated for each specimen as the area under the load versus displacement curve up to the displacement at break, is normalized with respect to the resistant section of the specimen and plotted against the specimen ligament length, l. The experimental data are then linearly interpolated according to the relationship:[16,17]

$$w_f = \frac{W_f}{lB} = w_e + \beta w_p \cdot l \qquad (4)$$

where B is the specimen thickness, β a shape factor depending on both the material and the geometry of the specimen, and w_f, w_e and w_p are the specific total, essential, and nonessential work of fracture, respectively. The term w_e represents the energy (per fracture surface unit) dissipated in the facture process zone, whereas, βw_p is the density of the energy dissipated by deformation processes that occur in the outer plastic zone away from the fracture surfaces. It has been proposed that w_e is an intrinsic material property that characterizes the material fracture resistance under plane-stress conditions. Recent studies have shown that the total fracture energy W_f can be divided into two components[28–30]: the work of fracture spent for yielding the ligament region W_y and the work of fracture for necking and subsequent tearing of the ligament region W_{nt}. Considering the yielding and necking/tearing contributions to w_f the following equations are obtained:

$$w_y = \frac{W_y}{lB} = w_{\text{ey}} + \beta_y w_{\text{py}} \cdot l \qquad (5)$$

$$w_{\text{nt}} = \frac{W_{\text{nt}}}{lB} = w_{\text{ent}} + \beta_{\text{nt}} w_{\text{pnt}} \cdot l \qquad (6)$$

where w_{ey} and w_{ent} are the yielding and necking/tearing components of the specific essential work of fracture w_e respectively, w_{py} and w_{pnt} are the yielding and necking/tearing related parts of the specific nonessential work of fracture w_p respectively, whereas β_y and β_{nt} the yielding and necking/tearing related parts of the shape factor β respectively.

Data of EWF testing are reported in Figure 6(a–c) for octamethyl-POSS/PP blends at 0, 3, and 10 wt % POSS, respectively.

By comparing the load versus displacement curves of the various materials examined, it emerges that the presence of octamethyl-POSS particles within PP tends to prevent the material fracture instability that appears very pronounced for neat PP. Further, visual inspection of the tested specimens showed that full yielding prior to crack propagation did not occur for PP at any ligament length examined, whereas for all the samples of the two POSS/PP blends, the ligament region was completely yielded prior to crack growth and full yielding of the ligament region occurred at about the maximum load. Nevertheless, though the specimens of the blends at 3 and 10 wt % POSS showed yielding followed by ductile tearing, all the samples of the system at 3 wt % POSS as well as the samples labeled (a) and (b) of the blend at 10 wt % POSS exhibited fracture instability [see Fig. 6(b,c)]. Further, from Figure 6(b,c) it emerges also that the load versus displacement curves relative to the blends at 3 and 10 wt % POSS showed an appreciable homothetic behavior with varying ligament length, as expected in EWF testing, at least up to the completion of the yielding of the ligament region. It is worth noting that, by comparing for the two different POSS-based systems the curves concerning with similar ligament length (l = 2.32 mm), the higher is the POSS content in the material, the lower is the maximum load. This result is in agreement with the tensile strength data obtained by uniaxial tensile tests, which indicate that the yield stress decreases by increasing the POSS content (see Table III).

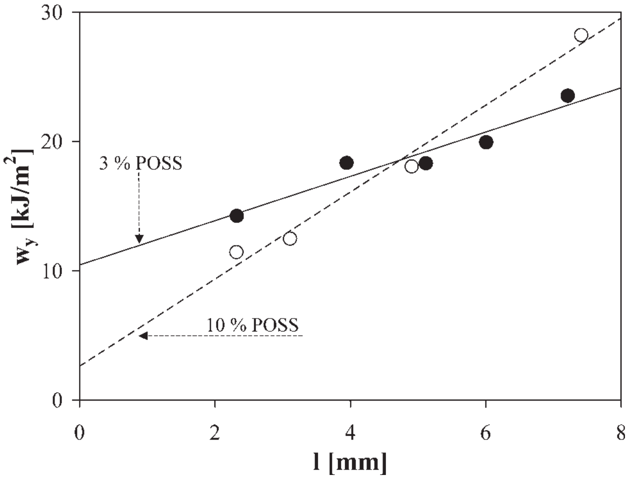

Figure 7 Yielding contribution (w_y) to the specific work of fracture as a function of ligament length (l) for the octamethyl-POSS/PP blends with 3 (filled symbols) and 10 (open symbols) wt % of POSS; the least square regression lines fitted on each series of experimental data are also traced (see text); % stands for wt %.

TABLE IV
Essential Work of Fracture Parameters (Yielding Components) for the Octamethyl-POSS/PP Blends

POSS content (wt %)	w_{ey} (kJ/m^2)	$\beta_y w_{py}$ (MJ/m^3)
3	10.4	1.7
10	2.6	3.4

Thus, the occurrence of fracture instability and the incomplete yielding of the ligament region prior to crack propagation do not permit the application of the EWF methodology for the evaluation of the intrinsic material fracture resistance w_e for any system examined in this work. However, for the octamethyl-POSS/PP systems at 3 and 10 wt % POSS, by considering that for all the samples the full yielding of the ligament region prior to crack growth was ascertained, the yielding component (w_{ey}) of the specific essential work of fracture could be determined. For the evaluation of w_{ey}, the total work of fracture W_f was divided for each specimen into two parts: work of fracture for yielding W_y (area under the load versus displacement curve up to the displacement corresponding to maximum load) and work of fracture for necking/tearing W_{nt} (remaining area). By plotting w_y versus l of each series of specimens, the values of w_{ey} and $\beta_y w_{py}$ were determined according to eq. (5) as the intercept at zero ligament length and the slope of the least square regression line fitted on the experimental data, respectively (see Fig. 7).

The results, reported in Table IV, indicate that the system containing 10 wt % octamethyl-POSS is characterized by a remarkably lower value of the yielding component (w_{ey}) of the specific essential work of fracture with respect to the blend with 3 wt % POSS. This means that the system at 3 wt % POSS, as far as the yielding phase involved in the fracture process is concerned, exhibits a higher resistance than the other blend. In spite of the abatement of w_{ey}, the system containing 10 wt % POSS exhibits a higher $\beta_y w_{py}$ value than the other POSS/PP blend. This indicates that, in the fracture process, during the yielding phase, the energy globally dissipated by the deformation processes occurring in the outer plastic region surrounding the fracture process zone is higher for the system with 10 wt % octamethyl-POSS than for the material at 3 wt % POSS.

CONCLUSIONS

The mechanical behavior of POSS/PP blends is largely affected by the length of the POSS alkyl chains. POSS particles bearing short hydrocarbon residues like octamethyl-POSS exert a reinforcing action (stiffness) when dispersed in the PP matrix and, on the other hand, they induce a decrease in the material yield stress, while the presence of long substituents as in isooctyl-POSS induces a reduction of both Young's modulus and mechanical strength. The effective area model developed by Ishai and Cohen, usually applied to rubber-filled polymers, can account for the reduction of the yield strength observed in isooctyl-POSS/PP and octaisobutyl-POSS/PP blends in comparison with neat PP. Also, the decrease in Young's modulus exhibited by isooctyl-POSS/PP blends can be qualitatively explained using a simple micromechanical model proposed by Kerner for rubber-filled polymers. Therefore, in our opinion, the mechanical behavior of the POSS/PP blends investigated in this work can be interpreted by considering POSS as particles with a siliceous hard-core embedded in a hydrocarbon soft-shell, which limits the stress transfer from the matrix to the core. Since the thickness of the soft-shell increases with the length of the alkyl groups, POSS bearing long substituents can be assumed to have the same effect as rubber inclusions. However, the predictive capability of the micro-mechanical models mentioned above fails when the presence of POSS induces a modification of the matrix morphology, as in the case of the blend with 10 wt % octaisobutyl-POSS where, besides the α-form, which was the only crystalline phase observed in the other materials investigated, the occurrence of β and γ PP crystalline phases was evidenced.[14] Finally, the fracture tests highlighted that the progressive incorporation of octamethyl-POSS particles within PP makes the material more efficient in preventing fracture instability, with respect to neat PP.

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