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Specific Properties of *In Situ* Ruthenium-Catalyzed Polyamide 12/Polydimethylsiloxane Compatibilized Blend

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ABSTRACT: The main objective of this work focused on the chemical modification of polyamide 12 (PA12) properties through the reaction with a hydride-terminated polydimethylsiloxane (PDMS-SiH). The investigated PA12/PDMS-SiH blend was compatibilized by ruthenium derivative catalyzed hydrosilylation reaction in molten state. This original route enhanced interfacial adhesion and avoid PDMS-SiH leaching phenomenon between the two immiscible phases. More specifically, the size of PDMS-SiH domains in the blend decreased from around 4 μm to 800 nm and from 30 to 1 μm after compatibilization with 10 and 20 wt % PDMS-SiH, respectively. For the best compatibilized PA12/PDMS-SiH blend, the introduction of PDMS lowered the surface free energy and the PA12-based blend turned from hydrophilic to hydrophobic behavior, as evidenced

by the water contact angle measurements. Gas permeability and CO_2/H_2 and CO_2/He gas selectivity were also improved with the increase in PDMS content. Besides, the mechanical properties were enhanced with 13% increase in Young's modulus after *in situ* compatibilization with 15 wt % PDMS-SiH. Thermal stability was also improved after compatibilization as the initial degradation temperature of reactive blends obviously increased compared with nonreactive ones.

KEYWORDS: extrusion; gas permeability; gas permeation; hydrosilylation; polyamide; polyamide 12; polydimethylsiloxanes; polymer blend; polysiloxane; surface free energy

INTRODUCTION Polydimethylsiloxanes (PDMSs) are of particular interest as they have a wide range of commercial applications resulting from their special properties,^{1,2} such as high chemical and thermal stability, low toxicity, hydrophobicity, high gas permeability, and so on. Due to these specific properties, the introduction of PDMS to other kinds of polymers was widely studied to improve their related properties especially hydrophobicity and gas permeability. To realize such improvements, synthesis of PDMS-based copolymers are widely reported. Ho et al.³ synthesized poly(dimethylsiloxane-urethane-urea) (PDMS-PUU) block copolymers based on aminopropyl endcapped dimethylsiloxane [$\text{H}_2\text{N}(\text{CH}_2)_3(\text{Si}(\text{CH}_3)_2\text{O})_n\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{NH}_2$], isophorone diisocyanate [5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane] and 1,4-benzenedimethanol by a two-step polymerization. The surface properties of various segmented block copolymers had been studied using dynamic contact angle (CA) analysis. It was shown that the surfaces reorganized by a mechanism in which the hard block urethane-urea domains migrated through the soft block silicone to the polymer-water interface, and this copolymer established development of nontoxic, antifouling coatings for use in marine environments. Miyata and coworkers⁴ also synthesized

different kinds of membranes, consisting in ethanol-permeable PDMS and water-permeable poly(methylmethacrylate) (PMMA), using PDMS macro-azoinitiator initiating the addition reaction between vinyl-ester terminated PDMS and MMA in solution. The copolymers were prepared into membranes to investigate the relationship between their microphase separation and their permselectivity for aqueous ethanol solutions during pervaporation. They found that the PMMA-*g*-PDMS membranes changed from water- to ethanol-permeable at a PDMS content of 35 mol %.

Syntheses of such PDMS containing copolymers are useful but not widely used solution to combine them to other kinds of polymers due to the high cost and complex synthesis steps. In recent years, polymer blending process^{5,6} seems to be more potential route to realize thermoplastic modification based on PDMS. However, for most of such polymer blends, the immiscible problem is obvious, due to the low surface tension and low viscosity of PDMS.¹ To obtain stable materials, there are two common routes for polymer blends compatibilization, one of them is adding amphiphilic copolymer which can work as interfacial agent to promote interface stability. As represented by Xu et al.,⁷ a proportion of PE-*b*-

PDMS diblock copolymer achieving through the esterification reactions between monohydroxy-terminated poly(dimethylsiloxane) (PDMS-OH) and the corresponding carboxyl terminated polyethylene (PE-COOH) in the presence of tetrabutyl titanate was used as a compatibilizer in the blends of high-density polyethylene (HDPE) and silicone oil. 1 wt % of the copolymer promoted the dispersion of silicone oil in HDPE going from more than 5 μm silicone oil dispersed domains to no obvious phase segregation approaching by SEM observation and improved the mechanical properties of HDPE/PDMS blends. Besides, there has been recent interest in reactive blending. During the process, polymers have reactivity with each other and can react to achieve *in situ* compatibilization.⁸ This method is effective to control morphology and to design new materials without previous compatibilizer synthesis. For example, as reported by Zhou and Osby,⁹ they obtained polycarbonate (PC)/PDMS compatibilized blends by using hydroxyl-terminated PDMS (PDMS-OH) which reacted with PC through twin-screw extrusion at 280 °C. The newly formed PC-PDMS copolymer provides a compatibilization effect for the stable submicron blend morphology in an otherwise immiscible PC/PDMS blend system. Silicone material was found to be well dispersed in the PC major phase forming small spherical domains with the domain size of about 0.2–0.9 μm . Such PC/PDMS blend was proved to have excellent low temperature impact toughness.

Our work was inspired by our earlier study conducted by Bonnet et al.¹⁰ They developed a new and original reactive blending between Ethylene-vinyl acetate copolymer (EVA) and PDMS based on $\text{Ru}_3(\text{CO})_{12}$ catalyzed EVA carbonyl hydrosilylation by Si—H groups of hydride-terminated PDMS (PDMS-SiH). The occurrence of the hydrosilylation reaction at the EVA/polysiloxane interface promoted a homogenization of the blend. The method was also successfully applied to polyester polybutylene terephthalate (PBT) and polymethylhydrosiloxane (PMHS)¹¹; it formed stable crosslinking network after reactive blending. The PBT/PMHS blend showed slight improvement in hydrophobicity compared with pure PBT. More recently, the $\text{Ru}_3(\text{CO})_{12}$ catalyzed reactive blending was extended from polyester to polyamide which was never been reported.¹² Through model study, it confirmed the possibility and efficiency of ruthenium catalyzed amide hydrosilylation reaction, concentration of N-silylated compounds can reach 70 mol % after 2 h reaction at 100 °C. Then the amide hydrosilylation reaction was extended to the reactive blending of polyamide 12 (PA12) with PDMS-SiH under molten processing conditions. The occurrence of such reaction at the interface between PA12 and PDMS-SiH was proved, N-silylated copolymers formed at the interface and worked as compatibilizer. Therefore, a structured PA12/PDMS blend was investigated by rheology and electronic microscopy at different scales. Specifically, the dispersion of PDMS domains decreased from 3 to 4 mm to around 0.8 mm in diameter forming submicronic morphology. In the meantime, PDMS-SiH oxidation reaction was partially observed under such reactive conditions and led to a second PDMS gel-based dispersion with a diameter of

approximately 20–30 nm. Therefore, we proved that ruthenium-catalyzed amide hydrosilylation provided an original, efficient, and controllable route for PA12/PDMS compatibilization. As mentioned before, the introduction of PDMS to other kinds of thermoplastics were aimed to lead properties modification. The main objective of this part of work focused on the hydrophobicity, gas permeability, and mechanical properties modification of PA12 with different proportions of PDMS and investigated related impact factor and mechanism.

EXPERIMENTAL

Materials

Polyamide 12 (PA12) was supplied by Arkema (AESNO TL RILSAN). The melting point is 170 °C, number average molar mass M_n is 26,000 g mol^{-1} , weight average molar mass M_w is 47,000 g mol^{-1} , and the density is 1.01 g cm^{-3} at room temperature.

Hydride-terminated PDMS (PDMS-SiH) with a molar mass of 726 g mol^{-1} and triruthenium dodecacarbonyl [$\text{Ru}_3(\text{CO})_{12}$] were commercial products from ABCR. Moreover, viscosity ratio of PDMS-SiH and PA12 ($\lambda_{\text{PDMS-SiH/PA12}}$) is 3×10^{-7} , and the molar ratio of functional groups $[\text{SiH}]/[-\text{CONH}]$ is 6.7×10^{-2} .

Processing of PA12/PDMS-SiH Blends

PA12 pellets were dried in vacuum at 80 °C for 24 h. Melt reactive processing of PA12 and PDMS-SiH was carried out in a Haake Plasticorder intensive batch mixer equipped with a Rheomix 600 internal mixer. The temperature of the mixer chamber was set at 170 °C and the rotation speed was 50 rpm. The resistant torque and temperature were monitored during whole process. In a typical experiment, dried PA12 was added in the mixer chamber and first mixed for 3 min to melt the polymer until the torque curve reached a plateau. Then, the catalyst and PDMS-SiH mixture with a predetermined composition (Table 1) was added in the molten PA12 with a syringe. Furthermore, nonreactive PA12/PDMS-SiH blend and pure PA12 were prepared with the same processing as references.

Samples for mechanical measurement were prepared using a 15 g-capacity DSM microextruder (Midi 2000 Heerlen, NL) with corotating screws (length/diameter (L/D) ratio = 18). PA12 pellets were added in the extruder first, then PDMS-SiH and catalyst mixture were added with a syringe from the top gap between the screw and chamber surface. The blends were processed at 200 °C for 5 min under a 100-rpm speed and injected in a 10 cm^3 mold at 80 °C to obtain dumbbell-shaped specimens (ISO 527-Type 5A: dumbbell-shaped, $25 \times 4 \times 2 \text{ mm}^3$). In addition, we confirmed by SEM that the processing methods (Haake plasticorder and micro-extruder) have no effect on the final morphologies.

Methods of Characterization

The morphology of the polymer blend was first characterized by scanning electron microscopy (SEM) using a FEI QUANTA 250 microscope with an accelerating voltage of 10 KV. The

TABLE 1 Composition of the PA12/PDMS-SiH Polymer Blends

	Sample	Designation	m(PA12):m(PDMS-SiH):m(Catalyst)
Internal mixer	PA12-PDMS-SiH (10%)-nonreactive	PA12:PDMS-SiH	90:10
	PA12-PDMS-SiH (10%)- reactive	PA12:PDMS-SiH:catalyst	90:10:1
	PA12-PDMS-SiH (20%)- reactive	PA12:PDMS-SiH:catalyst	80:20:1
Micro-extruder	PA12-PDMS-SiH (10%)-nonreactive	PA12:PDMS-SiH	90:10
	PA12-PDMS-SiH (10%)-reactive	PA12:PDMS-SiH:catalyst	90:10:1
	PA12-PDMS-SiH (10%)-reactive	PA12:PDMS-SiH:catalyst	85:15:1

samples were prepared in two different ways, either fractured in liquid nitrogen or a smooth flat surface of these was obtained by cryo ultramicrotomy at $-155\text{ }^{\circ}\text{C}$ with a UC7 LEICA ultramicrotome. Then the surfaces were coated with a gold/palladium thin layer of 10 nm. The morphology was also examined by transmission electron microscopy (TEM). Ultrathin sections of about 80 nm from samples, taken in triplicate throughout the whole materials, were cut by cryo ultramicrotomy at $-155\text{ }^{\circ}\text{C}$ and observed using a PHILIPS CM120 microscope operated at an accelerating voltage of 120 KV.

Differential scanning calorimetry (DSC) measurements were performed on a Q20 (TA instrument) from 30 to 200 $^{\circ}\text{C}$ for PA12 and PA12/PDMS-SiH blends. The samples were kept for 3 min at 200 $^{\circ}\text{C}$ to erase the thermal history before being cooled and then heated at a rate of 10 $^{\circ}\text{C min}^{-1}$ under Helium flow 40 mL min^{-1} . The crystallinity was calculated using the melting enthalpy for a 100% crystalline yield to PA12 of 95 J g^{-1} .¹³

Thermogravimetric analysis (TGA) measurements of PA12 and PA12/PDMS-SiH blends were performed on a TA Q500 at a heating rate of 10 $^{\circ}\text{C min}^{-1}$. The samples were heated from 30 to 700 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C min}^{-1}$ under helium flow.

Rheological measurements of the samples were carried out using a Rheometer ARES. The samples were first molded as disk ($d = 25\text{ mm}$, $h = 1\text{ mm}$). The samples were heated at 200 $^{\circ}\text{C}$ for 5 min until equilibrium was reached and the gap between the two plates was adjusted to 1 mm. Then the samples were equilibrated for 2 min before starting the test. Nitrogen gas was used to prevent thermal oxidation of the samples. The linear complex shear modulus ($G^*(\omega) = G'(\omega) + jG''(\omega)$, $j^2 = -1$) was measured at 200 $^{\circ}\text{C}$.

Uniaxial tensile tests of PA12/PDMS-SiH blends were performed at room temperature in a Shimadzu universal testing machine model AG-10 KN, speed of 30 mm min^{-1} until fracture. For calculation of the elasticity modulus, speed of 2 mm min^{-1} was used, using segment mode between 0.05 and 0.25% of strain (among elastic deformation). The tabulated results are average of at least five measurements.

The water uptake measurements were carried out after 12-day long immersion of test samples (hot pressed film, thickness: around 0.5 mm) in distilled water, at room

temperature. It was checked that this immersion time was high enough to reach water sorption equilibrium for all studied samples.

Surface free energy of modified PA12 was determined at room temperature with the sessile drop method using a Dataphysics Digidrop CA meter equipped with a CDD2/3 camera. From CA, measurements performed with water ($\gamma_l = 72.8\text{ mN m}^{-1}$, $\gamma_l^d = 21.8\text{ mN m}^{-1}$, $\gamma_l^p = 51\text{ mN m}^{-1}$) and diiodomethane ($\gamma_l = 50.8\text{ mN m}^{-1}$, $\gamma_l^d = 48.5\text{ mN m}^{-1}$, $\gamma_l^p = 2.3\text{ mN m}^{-1}$) as probe liquids on films with smooth surface; polar and dispersive components of surface free energy were determined by using Owens-Wendt theory.¹⁴ The tabulated results are average of at least five measurements on different parts of each sample.

Gas permeation experiments were carried out for He, H₂, and CO₂ at 20 $^{\circ}\text{C}$ under an upstream pressure equal to 3 bars. The permeation cell consisted of two compartments separated by the studied membrane. A desorption step under secondary vacuum was performed before each permeation experiment. The gas permeability coefficient (P) was calculated from the gas flux measured in the steady state (J) according to the following equation:

$$P = \frac{LJ}{\Delta p} \quad (1)$$

where L is the thickness of the film and Δp is the pressure difference between the two cell compartments. The permeability coefficient, P , expressed in barrier unit (1 barrer = $10^{-10}\text{ cm}^3(\text{STP})\text{ cm cm}^{-2}\text{ s}^{-1}\text{ cm Hg}^{-1} = 7.5 \times 10^{-18}\text{ Nm}^3\text{ mm}^{-2}\text{ s}^{-1}\text{ Pa}^{-1} = 3.348 \times 10^{-16}\text{ mol mm}^{-2}\text{ s}^{-1}\text{ Pa}^{-1}$) was calculated from the slope of the straight line in the steady state. The precision on P values was better than 5%.

RESULTS AND DISCUSSION

Processability and Morphological Behavior

In our previous work, the reactive compatibilization of PA12/PDMS-SiH has been successfully proved in molten conditions under shear.¹² The formation of N-silylated polyamide and polyamine at the interface, as illustrated in the Figure 1, allowed to increase the interfacial adhesion between the two immiscible polymers, and finally promoted the dispersion of PDMS-SiH into the PA12 matrix.

FIGURE 1 Scheme of reaction between PA12 and PDMS-SiH and variation in the torque between PA12 and PDMS-SiH (10 wt %) under shear in the internal mixer at 170 °C: reactive blending (solid line) and nonreactive blend (dotted line). [Color figure can be viewed at wileyonlinelibrary.com]

In the Figure 1, the evolution of the system morphology can be associated to the variation in torque during polymer blending. It is clear that after the introduction of PDMS-SiH to molten PA12, the torque value decreases due to the PDMS-SiH lubrication. Then it increases to around 17 Nm for

both in nonreactive¹⁵ and reactive system. As reported by Scott and Macosko as well as Cassagnau and Fenouillot,^{16,17} the mixing torque variation is primarily due to the change in blend rheology caused by a morphological transformation in such blend. For nonreactive blend, the torque variation keeps steady after the slight increase and we can observe from SEM analysis [Fig. 2(a)], for such nonreactive blend, PDMS-SiH domains with a diameter around 3 μm dispersed in the PA12 matrix. This means the occurrence of weak mixing in such immiscible blend despite the extremely low viscosity ratio due to the low molar mass (726 g mol^{-1}) of PDMS-SiH.¹⁸ On the contrary hand, the torque value of PA12/PDMS-SiH reactive blend does not reach a steady plateau as for the nonreactive one but it increases rapidly from 17 to 53 Nm before decreasing again as shown in Figure 1. The torque variation corresponds to the variation in the apparent viscosity of the bulk material and consequently to some relevant microstructure development.^{13,17,19} Comparing the morphology (Fig. 2), it is clear that in presence of catalyst, new formed copolymers such as N-silylated polyamide and N-silylated polyamine act as compatibilizer. The mixing became effective and the morphology changed drastically until the torque reached a plateau. Then the torque decreased and finally compatibilized stable blend with a decrease in the PDMS-SiH domain size (around 0.8 μm) and narrow domain size distribution of PDMS-SiH in PA12 matrix is obtained. In addition, during the process, a second PDMS gel based

FIGURE 2 Representative SEM morphology: (a) PA12/PDMS-SiH (10%)-nonreactive, (b) PA12/PDMS-SiH (10%)-reactive, (c) PA12/PDMS-SiH (20%)-reactive, (d) TEM morphology of PA12-PDMS-SiH (10%)-reactive blend. [Color figure can be viewed at wileyonlinelibrary.com]

dispersion with a diameter of approximately 20–30 nm is also formed due to self-oxidation¹² as shown in Figure 2(d).

As PDMS has a lot of unique properties, theoretically the more PDMS is introduced, the more the modification of organic polymer will be obvious as shown by Mackenzie et al.,²⁰ who found that the organically modified silicates take on a more flexible nature as the PDMS concentration was increased. But, as mentioned before, the PDMS-SiH acting as a lubricant, the shear rate was located in the PDMS-SiH fluid which coated the wall of mixing chamber. When the PDMS-SiH concentration is not high, effective mixing can be carried out. Along with the PDMS-SiH amount increasing, lubrication is more pronounced and there is only a part of PDMS which can be mixed into molten PA12. Even though the reaction is efficient, the formed compatibilizers were not in high concentration enough to promote the dispersion of whole PDMS as reported in some literatures.²¹ Thus, the whole addition of PDMS-SiH resulted in a poor mixing, and the blends remain totally separated at the macroscale (the PDMS-SiH leads to an oily surface). In our processing conditions, it was possible to increase PDMS-SiH content up to 20 wt %, but in a specific route. At first, we added 10 wt % PDMS-SiH and catalyst mixture in the molten PA12. In such conditions, efficient reactive blending was observed. When the torque has reached a steady plateau, another 10 wt % of pure PDMS-SiH (without catalyst) was introduced. The morphology of PA12/PDMS-SiH (20%)-reactive blend [Fig. 2(c)] proved the efficient blending, PDMS-SiH domains dispersed in the matrix with a diameter around 1 μm and a narrow distribution. In addition, through simply comparing 10 and 20 wt % PDMS-based blends morphology, we found a higher concentration of PDMS-SiH phase in the one with 20 wt % PDMS-SiH [Fig. 2(c)]. It should be mentioned that the sample is not oily like the one with poor mixing. Thereby, it was proved to be an efficient way to increase PDMS-SiH content by introducing it step-by-step.

The study of torque variation and related morphology confirmed the reactive compatibilization between PA12 and PDMS-SiH catalyzed by ruthenium catalyst. The *in situ* formed copolymers promote the dispersion of PDMS-SiH in PA12 matrix. Stable PA12/PDMS-SiH blends with a reduction in domains size and a narrow size distribution of PDMS-SiH phase was observed. Specifically, the size of PDMS domains of reactive blends with 10 and 20 wt % contents decreases to 0.8 and 1 μm , respectively. As the polymers compatibilization impacts the properties of the blend,²² the rheological, thermal, mechanical, and gas permeability properties were investigated to understand the morphology–property relationships of such PA12/PDMS-SiH blends.

Rheological Behavior

The rheological behavior of two-phase polymer blends is affected by the flow-induced changes in morphology. Compatibilizer leads to smaller domain size and narrower size distribution of the dispersed phase. In physical compatibilized blends (compatibilization through adding premade

copolymers), the rheological properties are influenced by the amount, molar mass, and the architecture of the compatibilizer.²³ Figure 3(a,b) shows typical behavior of the dynamic modulus for the pure matrix and the compatibilized blends. Results show that the two modulus of blends increase at low frequency, the storage modulus increases more rapidly than the loss one. The addition of PDMS-SiH in PA12 matrix significantly affected the frequency dependence of G' and G'' especially for compatibilized PA12/PDMS-SiH blend with higher concentration (20 wt %) of PDMS-SiH. It means the blends have additional relaxation process.^{24,25} As reported in the literature, this additional relaxation could be attributed to the shape-relaxation of drops²⁶ and the interfacial viscoelasticity of compatibilizer²⁷ in the blend.

But in this case only the shape relaxation cannot explain alone this viscoelastic behavior; there is also shear thinning behavior and yield stress behaviors at low frequency in Figure 3(c). Actually, this behavior is also attributed to the blend morphology at the nano-scale [Fig. 2(d)], to be more exact, nanostructure of PDMS (gel particles around 20–30 nm) formed through oxidation reaction and presented a second gel based nanostructure. Such nano particles dispersed in the blend and their amount increased with the increase in PDMS-SiH content. The effect of them to viscoelastic behavior is similar to nano-fillers, some of them can induce a decrease in interfacial tension and stabilized the blend. Both sharp relaxation of PDMS droplets and effect of PDMS nano gel particles should both be taken into account, but are still difficult to quantify for a complete understanding.

Thermal Properties: TGA

Blend compatibilization plays an important role in the degradation and thermal behavior of the blends.^{28,29} The comparison of thermal stability of PA12, PA12/PDMS-SiH nonreactive, and reactive is shown in Figure 4. The initial degradation temperature shifts toward higher temperature for the $\text{Ru}_3(\text{CO})_{12}$ catalyzed reactive blend in comparison with the noncatalyzed blend, which indicated that compatibilized blend is relatively more stable than the nonreactive one. More precisely, the weight loss at around 419 °C for nonreactive blend coming from the degradation of PDMS phase was no more observed for the reactive one. This indicated the improvement of PDMS phase stability in the blend, because the formed PA12-PDMS-SiH copolymer by hydrosilylation reaction enhances the interaction between phases.

Furthermore, as described before, a part of PDMS-SiH changes to gel-like nano particles due to oxidation reaction in the presence of ruthenium catalyst also leading to enhance the thermal stability. Our results are in agreement with observations of other researchers,^{28,30} such as Giri et al.²⁸ They found that the initial degradation temperature improved with the increase in *in situ* formed ethylene-methylacrylate (EMA)-*g*-PDMS copolymers concentration until reaching a maximum value (i.e., 332 °C for 0 wt %, 415 °C for 10 wt %, 416 °C for 12 wt %, and 415 °C for 14 wt %

FIGURE 3 Rheological behaviors as a function of frequency for PA12, PA12-PDMS-SiH (10%), PA12-PDMS-SiH (20%) reactive blends: (a) variation in storage modulus, (b) variation in loss modulus, and (c) complex viscosity. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

EMA copolymer). Such increase is also found in PA12/PDMS-SiH (20%) reactive blend, confirming that compatibilization also promotes the thermal stability even when the PDMS content increased. The residues of PA12/PDMS-SiH reactive blends at 700 °C are also more important than the ones for pure PA12 and PA12/PDMS-SiH nonreactive blend. As shown in Figure 4, the residue at 700 °C increases from 0.29 to 0.65 wt % for PA12/PDMS-SiH (10 wt %) nonreactive and reactive blends respectively and kept increasing with the increase in PDMS content (0.82 wt % for the one containing 20 wt % PDMS). Satyanarayana and Alper³¹ proved that in the presence of rhodium catalyst, PDMS formed crosslinking network which exhibited both higher thermal stability and residue.

Surface Free Energy

PDMS exhibits hydrophobic behavior and poor water wettability. The introduction of PDMS can modify the hydrophilic character of PA12. Such modification was proved by the change in surface free energy.

In this work, we used the Owens-Wendt theory which is the most general one used to determine the surface free energy¹⁴ basing on CA results of water and diiodomethane. PA12 and PA12-PDMS-SiH compatibilized blends show different wettability

depending on the different polarity of the two solvents. The static water and diiodomethane CA measurement results are shown in Figures 5 and 6 and Table 2. For pure PA12, the water CA is around $80 \pm 4.5^\circ$, thus less than 90° ; this last CA value being often considered to determine the limit between

FIGURE 4 TGA curves of pure PA12, PA12-PDMS-SiH nonreactive, and reactive blends under helium atmosphere. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

FIGURE 5 Water CA of pressed films: (a) pure PA12, (b) PA12-PDMS-SiH (10%)-reactive, (c) PA12-PDMS-SiH (20%)-reactive.

wettability and nonwettability.³² The PA12-PDMS-SiH compatibilized blends are both hydrophobic since the corresponding water CA are both larger than 90° and increased from $100 \pm 2.1^\circ$ to $106 \pm 1.8^\circ$ with PDMS content increasing from 10 to 20 wt %. For diiodomethane, an increase in CA is also observed as PDMS is introduced in the PA12 matrix. Specifically, the diiodomethane CA increased from $45 \pm 2.2^\circ$ for pure PA12 to $63 \pm 1.3^\circ$ and $68 \pm 1.5^\circ$ for compatibilized blends with 10 and 20 wt % PDMS content, respectively. It has to be noted that CA measurement was not carried out on nonreactive blend, since its surface appears oily caused by PDMS migration. Similar result was achieved by Zhang et al.,³³ who found a hydrophilic behavior for a phenoxy based polymer (water CA 74°) which changed to hydrophobic with a water CA 94° after the introduction of 1.7 wt % PDMS copolymer. They proved that the change in surface property is due to the surface enrichment of the low surface

energy component such as PDMS to minimize the overall surface free energy of the binary macromolecular system.

The surface free energy at room temperature^{34–36} was derived as follows (Table 2): pure PA12 38.0 mN m^{-1} ,³⁷ PA12-PDMS-SiH (10 wt %)-reactive blend 26.9 mN m^{-1} , and PA12-PDMS-SiH (20 wt %)-reactive blend 24.5 mN m^{-1} . Besides, there is also a decrease in both dispersive component (γ_s^d) and polar component (γ_s^p) of the surface energy. γ_s^d decreased from 33.0 to 26.1 mN m^{-1} (with 10 wt % PDMS) and to 24.3 mN m^{-1} (with 20 wt % PDMS). γ_s^p decreased from 5 mN m^{-1} for pure PA12 to 0.8 mN m^{-1} (with 10 wt % PDMS) and to 0.2 mN m^{-1} (with 20 wt % PDMS), respectively. It is clear that the introduction of PDMS significantly decreased the surface free energy of PA12.

FIGURE 6 Diiodomethane CA of pressed films: (d) pure PA12, (e) PA12-PDMS-SiH (10%)-reactive, (f) PA12-PDMS-SiH (20%)-reactive.

TABLE 2 Surface Properties of PA12 and PA12/PDMS Blends After Compatibilization

	$\theta_{\text{water}} (^{\circ})$	$\theta_{\text{diiodomethane}} (^{\circ})$	γ_s (mN/m)	γ_s^d (mN/m)	γ_s^p (mN/m)
PA12-pure	80 ± 4.5	45 ± 2.2	38.0 ± 1.3	33.0 ± 0.1	5.0 ± 1.2
PA12-PDMS-SiH (10%)-reactive	100 ± 2.1	63 ± 1.3	26.9 ± 0.5	26.1 ± 0.3	0.8 ± 0.2
PA12-PDMS-SiH (20%)-reactive	106 ± 1.8	68 ± 1.5	24.5 ± 0.4	24.3 ± 0.5	0.2 ± 0.1

The achievement of hydrophobicity due to PDMS introduction was also published in some literatures.^{38,39} For example, Chen et al.³⁹ prepared UV-curable PDMS-containing polyurethane (PU) oligomer (UV-PDMS-PU) where such UV-PDMS-PU system consisted in 1% (w/w) photo-initiator was coated either on PET or polyamide textile surface and then cured by UV-radiation. They found the washing stability of textile was improved due to the micro-phase separation of PDMS on the surface and improve its hydrophobicity. This mechanism is also suitable for our PA12-PDMS-SiH compatibilized blends, since SEM results confirm the micromorphology of the samples that PDMS with a diameter around 0.8 to 1 μm dispersed in PA12 matrix. This microstructure provides hydrophobicity to PA12-PDMS-SiH compatibilized blend.

Gas Permeability

PDMS as mentioned in the Introduction section is a polymer well known to have the highest gas permeability and diffusivity among all of the polymers manufactured on an industrial scale.^{40,41} Therefore, an increase in gas permeability is expected for the PA12-based materials with introduction of PDMS. The evolution of CO_2 permeability coefficients as a function of the blend composition is presented in Figure 7. As expected, the permeability increased as the PDMS content increased. However, significant differences were observed between the reactive and nonreactive PA12-PDMS-SiH blends. Higher permeability values were obtained for the reactive system. To discuss more deeply, the impact of the type of blends (noncompatibilized versus compatibilized) on the gas transport properties, we also indicated the permeability values calculated from Maxwell law in the Figure 7.

The Maxwell model developed in 1954,⁴² originally used for electrical conductivity of particulate composites, can be adapted to gas permeability of mixed materials membranes as eq 2:

$$\frac{P}{P_m} = \frac{1 + 2\phi(\lambda_d - 1)/(\lambda_d + 2)}{1 - \phi(\lambda_d - 1)/(\lambda_d + 2)} \quad (2)$$

where P is the effective permeability of the blend, P_m is the permeability of the continuous phase (PA12 matrix), ϕ is the volume fraction of the dispersed phase, known as loading, λ_d is the permeability ratio P_d/P_m , where P_d is the permeability of the dispersed phase (PDMS).

The permeability coefficient values determined on both systems (reactive and nonreactive blends) are lying below the theoretical curve. Maxwell law was developed for ideal binary systems, meaning that it neither takes into account

an eventual modification of the matrix due to the presence of the dispersed phase nor potential interfacial effects.⁴³ The former factor can be important especially for semicrystalline polymer. Actually, the polymer crystalline regions are considered to be impermeable to small molecules such as gases and thus change in crystallinity degree can lead to a modification of the final permeability. However, in our case through the DSC analysis, we found no notable changes in PA12 crystallinity after the introduction of PDMS. The PA12 matrix still maintained its individual property and kept the crystallinity around 60%.

For the reactive PA12-PDMS-SiH system, *in situ* compatibilization took place leading to the coexistence of micrometer and nanometer sized PDMS rich domains dispersed within the PA12 matrix. One could expect a high gas diffusion rate in such materials due to the formation of more interconnected permeable phases. However, it was shown that PA12-PDMS-SiH interfacial interactions were reinforced in these systems. Moreover, the presence of crosslinked PDMS rich nanoparticles was also evidenced. These last phenomena have a detrimental effect on gas diffusion and could explain the slightly lower values of permeability obtained with respect to the theoretical ones. For PA12-PDMS-SiH nonreactive blend, it can be noticed that P_{CO_2} is 1.3 barrer. This value is lower than one of the reactive PA12-PDMS-SiH with

FIGURE 7 Evolution of the CO_2 permeability coefficient as a function of PDMS content in PA12/PDMS blends. ([trif]) is representative of P_{CO_2} of PA12-PDMS-SiH(10%)-nonreactive blend, ([sqf]) is representative of P_{CO_2} of PA12/PDMS-reactive blend. The dotted line is Maxwell theoretical value tendency of P_{CO_2} . [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Evolution of the relative permeability (CO_2 , He, and H_2) as a function of PDMS-SiH content. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

the same composition (1.6 barrer) and lower than the theoretical value (1.75 barrer). This is due to that without compatibilization, PDMS is easy to leach out and enrich on the blend surface driving by the significant difference between PA12 and PDMS. Therefore, there are only a part of PDMS actually dispersed in PA12.

The gas transport study was enlarged to H_2 and He for the reactive PA12-PDMS-SiH blend, and the relative permeability (the ratio of blend permeability to neat PA12 permeability) was reported for each gas and each blend composition in Figure 8. The relative permeability of H_2 and He is very close to each other, since these two gases have similar kinetic diameters of 2.34 and 2.65 Å,⁴³ respectively. Furthermore, gas permeability increases as a function of PDMS content. However, the CO_2 relative permeability values are always higher than those measured for He and H_2 . This result can be assigned to the high solubility (S) of CO_2 in PDMS resulting in a higher P , as in a fickian transport mechanism with D the diffusion coefficient.

$$P = SD \quad (3)$$

According to the literature,^{44,45} a penetrant's relative permeability in PDMS can be largely determined by its relative solubility. Specifically, the solubility of CO_2 in PDMS is much higher than the one of H_2 [1.29 and 0.05 $\text{cm}^3_{\text{STP}}/(\text{cm}^3 \text{ atm})$, respectively]. Different gas permeability coefficients of CO_2 ,

FIGURE 9 Typical stress-strain curves of PA12 and PA12-PDMS-SiH blends and zoom of elastic deformation. [Color figure can be viewed at [wileyonlinelibrary.com](#)]

He, and H_2 provides a potential application as gas selectivities for PA12-PDMS-SiH blends.

Mechanical Behavior

The mechanical properties of pure PA12, PA12-PDMS-SiH-nonreactive, and PA12-PDMS-SiH-reactive with different PDMS contents were carefully analyzed and shown in Figure 9 and Table 3 (10 and 15 wt %). First, the Young's modulus, elongation at break, and tensile stress decreases (50% elongation at break, 21% tensile stress, and 6% Young's modulus decrease) as PDMS is introduced without compatibilization comparing with pure PA12. As there is no change in the crystalline behavior of PA12 matrix, it is obvious that the decrease in mechanical properties is due to a weak interfacial adhesion between PDMS and PA12. This had been proved by a lot of researchers,^{46,47} such as Prakashan et al.⁴⁷ who found that PP/PDMS blend in the absence of compatibilizer was easy to cause debonding at the elastomer-matrix interface. On the contrary, PA12-PDMS-SiH blend after compatibilization shows higher Young's modulus (890 MPa) than pure PA12 (750 MPa) and PA12-PDMS-SiH nonreactive blend (700 MPa). The yield stress almost kept the same value before and after introduction of PDMS. The increase in Young's modulus is related to the *in situ* formed copolymers promoting the compatibilization and enhancing the interfacial adhesion. In addition, a part of PDMS changed from liquid to gel through oxidation reaction in the presence of $\text{Ru}_3(\text{CO})_{12}$ forming a second nano-size gel based dispersion,

TABLE 3 Mechanical Properties of PA12 and PA12-PDMS-SiH Blends

Sample Name	Young's Modulus (MPa)	Yield Stress (MPa)	Elongation at Break (%)	Tensile Stress (MPa)
PA12	750 ± 14	52 ± 0.3	160 ± 4	70 ± 0.6
PA12-PDMS-SiH (10%)-nonreactive	700 ± 25	53 ± 1.4	80 ± 10	55 ± 1.1
PA12-PDMS-SiH (10%)-reactive	890 ± 20	51 ± 0.8	130 ± 10	70 ± 1.1
PA12-PDMS-SiH (10%)-reactive	850 ± 21	50 ± 1.1	120 ± 9	65 ± 1.3

which also promotes the mechanical properties comparing with nonreactive blend. The decrease in elongation at break after introduction of PDMS especially for nonreactive blend is due to the defects causing by the significant difference of viscosity between PA12 and PDMS.

Through increasing PDMS content in PA12-PDMS-SiH compatibilized blend, the mechanical properties decreases slightly (5% for the Young's modulus and 7% for both the elongation at break and tensile stress) compared with PA12-PDMS-SiH (10 wt %)-reactive blend. This behavior had been discussed in some publications as Bremner et al.⁴⁸ who found that polyurethanes/PDMS blend existed an optimal level of PDMS concentration around 1.5–2%, leading to an enhancement of the mechanical properties. Over this concentration, phase separation of PDMS became significant leading to a decrease in the mechanical properties. Such behavior can be expected in our studied blend series, explaining the decrease in mechanical properties of PA12-PDMS-SiH (15 wt %)-reactive blend, because the size of PDMS domain increased with PDMS content increase which had been confirmed by SEM study.

CONCLUSIONS

Ruthenium-catalyzed hydrosilylation provides an original and efficient route to compatibilize PA12 and PDMS-SiH blend. As a result, dispersion of PDMS in PA12 matrix is promoted with increasing interfacial adhesion between the two immiscible phases compared with nonreactive blend. The introduction of PDMS phase to PA12 with a well and stable dispersion can significantly modify some properties of PA12. Through characterization, it is clear that PA12 was modified from hydrophilic to hydrophobic since related water CA increased from 80° to over 100°. Gas permeability, especially for CO₂ also improved comparing with pure PA12 due to the introduction of PDMS phase. In addition, the thermal stability of PA12-PDMS-SiH blends was enhanced after compatibilization with a similar initial degradation temperature as PA12 but an increase in solid residue due to the formation of N-silylated copolymers and PDMS self-crosslinking via oxidation. Besides, the mechanical properties are enhanced with 13% increase in Young's modulus after *in situ* compatibilization with 15 wt % PDMS-SiH due to compatibilization and formation of PDMS second gel-based nanostructure.

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