

Reconsideration of the Effects of a Coupling Agent in Talcum-Filled Plastics

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ABSTRACT: Structure and morphology of talcum-filled polyethylene (HDPE–talc) were studied to examine the nature of beneficial effects of commercial silane coupling agents. Effects of the additive on the structures of the blends with various talc contents were studied through differential scanning calorimetry (DSC) analyses. Mechanism of reinforcement by the flake-like filler were analyzed through both classical treatments and a percolation model. Results suggest that for the studied system, silane had changed properties of the filled plastics, mainly through enhancement in filler dispersion and modification of matrix morphology. Choice of silane as coupling agents was thus questioned for the filled polyolefins with relatively low cost-to-performance ratio. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1227–1236, 1998

Key words: HDPE–talc; coupling agents; percolation; representative reinforcing volume

INTRODUCTION

Filling polymers with mineral dispersions has long been a practice in the plastics industry as a way to reduce production costs and to enhance certain properties.¹ Flake-like fillers, for example, talcum, are especially among interest because of their reinforcing potential. High aspect ratio and relatively low price of the fillers are very attractive in a plastics market that grows more and more competitive. Unfortunately, the better stiffness obtained through filling is often accompanied by drawbacks, such as worse processibility and lower toughness. To overcome these problems, a variety of methods were adapted, including the

choice of processing aids and modification of the filler surface. Based on the reasoning that the proper interlayer results in a balance between toughness and strength, the past decade has seen active efforts in developing new coupling agents and elastomer coatings for the fillers,^{2–4} many of which yield plastics with balanced performance.

However, properties of a filled system relies also on filler dispersion and matrix morphology, besides interfacial structure. While knowledge about interfacial structure in filled thermoplastics is still poor compared to their thermosetting counterparts,^{5,6} the disordered nature of filler dispersion and the complex structure of the crystalline matrix also make it very difficult to predict performances according to constituents in a reliable way. While surface treatments do affect interfacial structure in the products, such an influence occurs through processing, during which changes in other aspects are also inevitable.² Had effects of such treatment on dispersion and matrix morphology been more important than that on in-

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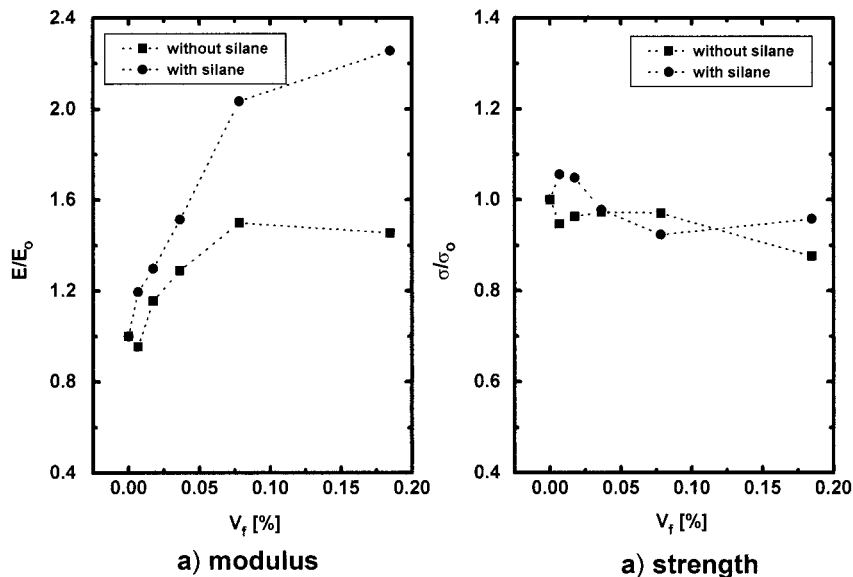


Figure 1 Tensile (a) modulus and (b) strength of HDPE-talc blends at various volume contents of filler.

terfacial structure, it would not be reasonable to use expensive coupling agents, such as silanes, titanium esters, and block copolymers, to make such filled plastics that have a relatively lower performance-to-cost ratio. A more economic practice might well be proper selection of fillers, processing aids, and resins or commercial polymer blends. In fact, chlorination before filling was proved superior to silane treatment in promoting

reinforcement in polypropylene.⁷ Effects of silane in such filled systems, therefore, remains to be understood more properly.

For this purpose, polyethylene-talcum blends was chosen for simplicity. Because there have already been extensive experimental results, which focused on the effects of composition on the rheological and mechanical properties of filled plastics in literature, analyses of the limited experimental

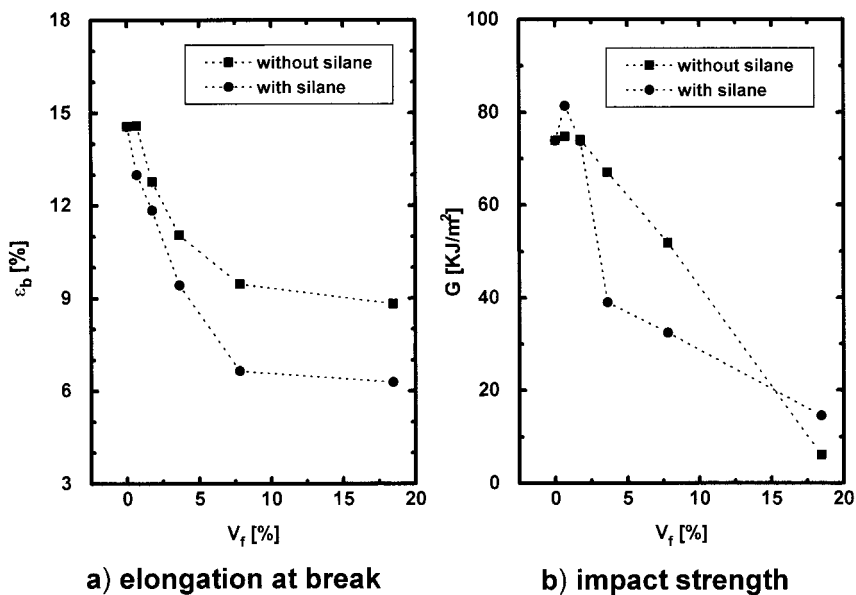


Figure 2 Toughness of the HDPE-talc blends.

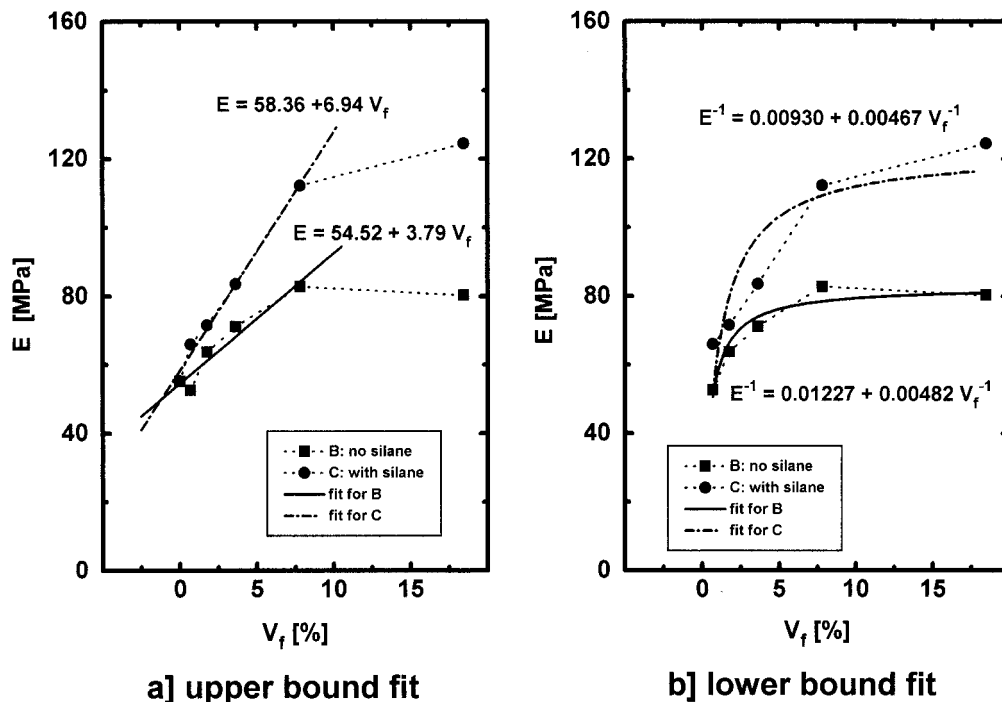


Figure 3 Upper- and lower-bound fits for tensile modulus.

results are emphasized in the present work, rather than repetition of works in the literature.

EXPERIMENTAL

Materials and Compounding

Polyethylene used was a commercial resin for high-speed cable coating, which consisted of two miscible grades of high-density polyethylene (HDPE) and enough antioxidants. The resin was mixed on a two-roll mill with 1250 mesh quality commercial talcum, which had been claimed to be identical to the hydrophobic Montana talc. The amount of the silane was kept at two percent of the weight of talc. The compounded sheets were compression-molded into 4 mm plates at 190°C. The cooling process was controlled by transferring the mold to a cold press. A similar procedure was used to prepare blends of neat polyethylene and silane. Great care has been taken to keep processing conditions identical. Annealing was performed in a air-ventilated oven at 85°C ± 1 when necessary.

Test and Characterization

Tensile and impact experiments were performed on 120 × 10 × 4 mm specimens following the Chi-

nese national standard GB1040-79, and on 55 × 6 × 4 mm unnotched in-plane specimens according to GB1043-79, respectively. Thermal analyses of above specimens were carried out with a Perkin-Elmer DSC-2 differential scanning calorimeter. Samples had been prepared by cutting a slice across each plate and heated in the DSC chamber to 190°C to eliminate the effects of previous thermal history and possible cold flow in slicing. Cooling and subsequent heating curves were recorded with a 10°C/min rate.

RESULTS AND DISCUSSION

Effects of Silane Coupling Agents on Tensile Properties and Impact Resistance

Figures 1 and 2 show mechanical properties of blends of HDPE with both treated and untreated talc. It can be seen that the presence of the silane coupling agent results in higher tensile modulus, lower strain at breakage, and almost unchanged tensile strength. Change in impact strength, the magnitude of which is smaller than that of the modulus, can be found to be highly dependent on talc content. These results agree well with the common sense¹ that talcum is a relatively good

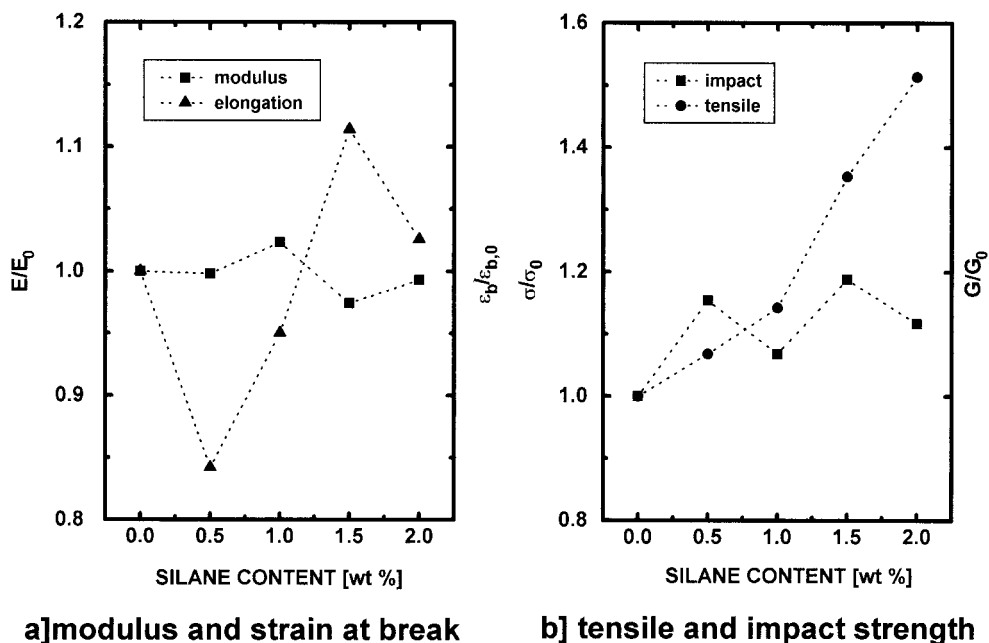


Figure 4 Normalized properties of HDPE-silane blends.

filler because it raises modulus while leaving strength unchanged.

For silane in the blends, talc may either enhance interfacial interaction, increase filler dispersion and/or modify matrix properties; whether it has raised stiffness through promoting interfacial interaction remains to be further checked through the dependency of the modulus on the talc content. From Figure 3(a), it can be seen that tensile moduli of both blends increase linearly with talc content, with exceptions at the highest talc content studied. For this upper bound fit of the $E \sim V_f$ relationship had been based on an assumption of uniform strain,^{8,9} a larger slope found in the system with silane could only indicate that more filler particles had shared the load than in blends without the additive. Moreover, the extrapolated value at zero talc content E_0 reveals another aspect of reinforcing mechanism, that is, possible changes in matrix stiffness. The value can be found to be larger in the silane-treated systems than that in the untreated ones, suggesting the silane could have enhanced matrix stiffness.

An alternative way to correlate modulus with filler content was through linear fit of E^{-1} versus V_f^{-1} . Such a lower-bound fit, based on an assumption of uniform stress behavior, however, was obtainable only with much larger scattering [Fig. 3(b)]. Although it covers the whole studied range of talc content, the large scattering of this appar-

ent fit indicates that it cannot be taken as evidence that the silane treatment had resulted in any stiffer interphase. In fact, it had been discovered that moduli of talc-filled plastics tend to follow the upper-bound rule more frequently.¹ Considering that both the lower- and upper-bound theories are two-phase models that describe macroscopic behaviors, they yield no more than average dependencies of modulus on filler content. Higher stiffness of the reinforcement phase found for the talc-treated blend in Figure 3(a) may well suggest that more filler had been under-stress, as has been revealed through the upper-bound fit.

Effects of Silane on Properties of the HDPE Matrix

Figure 4 shows the effects of silane on tensile and impact properties of neat HDPE. Compared to impact strength and tensile strain at break, tensile modulus and strength have to be considered unchanged in the content range studied here. It can be found from Figure 4 that strain at break, ϵ_b , changes with filler content in a less monotonous way, while impact strength increases more profoundly. It would be even more interesting to find that when silane content changes from 0.5 to 1.5%, the concentration of practical meaning; both ϵ_b and impact strength increases with that of the content. The talc-filled plastics in the present work had a silane content ranging, to the most, from 0.04 to 1.3%, based on the amount of polyeth-

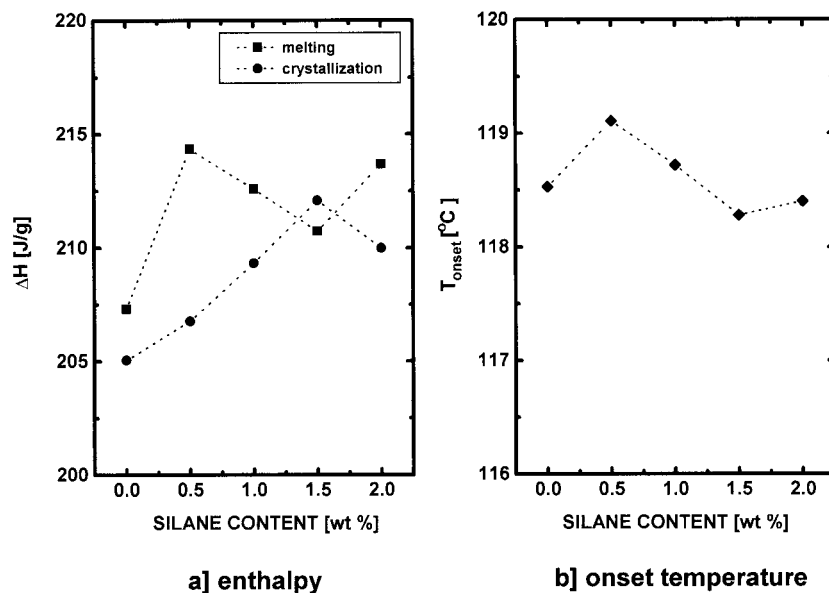


Figure 5 Effects of silane on melting and crystallization of HDPE.

ylene. Had the component been fully in polymer matrix, similar changes of matrix properties could be expected, which would no doubt affect macroscopic properties of the filled plastics.

Effects of Silane on Morphology of Polyethylene

Figure 5 shows the effects of the silane on the crystallization of neat HDPE. Higher enthalpy can be found in silane at all these contents of practical meaning. Moreover, crystallization enthalpy $-\Delta H_c$ increases [Fig. 5(a)] with the increase in silane content until the latter reaches a very high value of 1.5%, suggesting that the presence of the component must have accelerated crystallization of polyethylene at the lower cooling rate adopted in DSC scanning. In contrast, both the onset temperature of this crystallization T_{onset} [Fig. 5(b)] and the enthalpy of the following melting process ΔH_m decreased when the silane content increased from 0.5 to 1.5%. Compared to $-\Delta H_c$, the decrease in T_{onset} indicates that the accelerated crystallization here should have resulted from an increase in the mobility of polyethylene rather than from that in nucleation. The similar trend in $-\Delta H_c$, on the other hand, suggests that profound recrystallization and/or annealing must have occurred during the melting stage in DSC. During the precedent cooling stage, the presence of the silane had prevented polyethylene from forming crystallites as perfect and stable as in HDPE without the additive. As no accel-

erated nucleation at a higher temperature has been found, the increase in $-\Delta H_c$ and the decrease in ΔH_m must have something to do with phase separation in the HDPE–silane blend. Although dependency of the crystalline morphology on this phase separation remains to be studied further, the increase in toughness with that of silane content (Fig. 4) can be attributed to the imperfection of polyethylene crystallites caused by the presence of the additive. In the talc-filled systems, diffusion of the silane from the talc surface into polyethylene is unavoidable because of the higher temperature and the stress field during processing, provided that the silane molecules had not been all anchored chemically on the filler. Similar effects of silane on matrix morphology and properties, therefore, would be observed if enough of it could diffuse into matrix during processing.

Effects of Silane on the Morphology of the Filled Plastics

Figure 6 shows changes in crystallization and melting enthalpies of HDPE in its talc blends with the increase in filler content. It can be found that crystallization enthalpy ΔH_m tends to increase with that of talc content until the latter reaches 5%. The onset temperature T_{onset} can also be found higher in blends containing 2 and 5 wt % of talc than in the neat polyethylene [Fig. 7(a)]. The results agree well with the results on model systems of polyolefin–talc¹⁰ in that talc tends to nu-

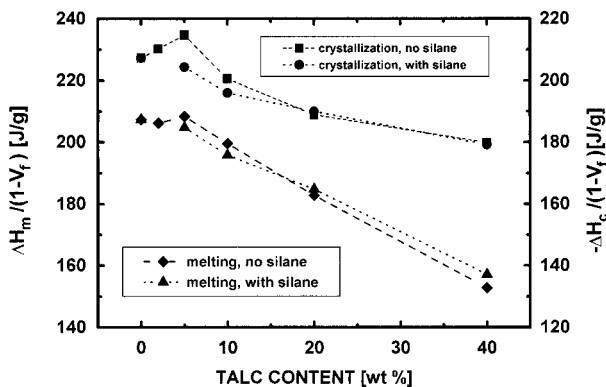


Figure 6 Melting and crystallization enthalpy of HDPE-talc blends.

create crystallization of polyethylene. In another words, an increase in ΔH_m had originated mainly from the nucleation role of talc. At higher talc contents, however, both ΔH_c and ΔH_m decrease with the increase in talc content. This suggests that effects of talc are more than simply nucleation. In fact, the offset temperature of the melting peak in DSC, T_{offset} , can be found to decrease generally with the increase in talc content in the same range, indicating a decreasing level of perfection of PE crystallites [Fig. 7(b)]. Restriction on chain movement imposed by the filler, therefore, must have played a certain role in determining the morphology of the matrix polyethylene.

With these two different mechanisms dominating the effects of talcum on PE crystallization, silane can be found playing different roles at dif-

ferent levels of filling load. As can be seen from Figure 6, both ΔH_c and ΔH_m are higher in blends containing silane up to a talc content of 10%. Compared to the effects of the additive on crystallization enthalpies of neat polyethylene found in one of the previous sections, the smaller ΔH_c in systems containing silane suggests that the additive should have been near the interface between PE and talc and, thus, prevented the filler from acting as nucleating agent; while lower ΔH_m in blends indicates that mobility of polyethylene must have been enhanced by the silane, which had diffused from interface into matrix during the melting stage of DSC scanning. In another words, the effects of silane on matrix morphology cannot be underestimated, even though the location of the additive could have been predominately near the interface.

At higher talc contents, different roles of the additive can be clearly seen through the slight, yet perceivable, decrease in the difference between the enthalpy of crystallization $-\Delta H_c$, and that of melting, ΔH_m , with talc contents. From Figure 8, it can be found that the enthalpy difference ($-\Delta H_c - \Delta H_m$) increases with talc content and is lower in blends with silane than in those without it. For the value ($-\Delta H_c - \Delta H_m$) characterizes the imperfection of crystallites formed in the DSC cooling stage, which primarily originated from volume restriction imposed by the filler in the present cases, the increase in ($-\Delta H_c - \Delta H_m$) with talc content reflects the loss of chain mobility; while the lower enthalpy difference in silane-

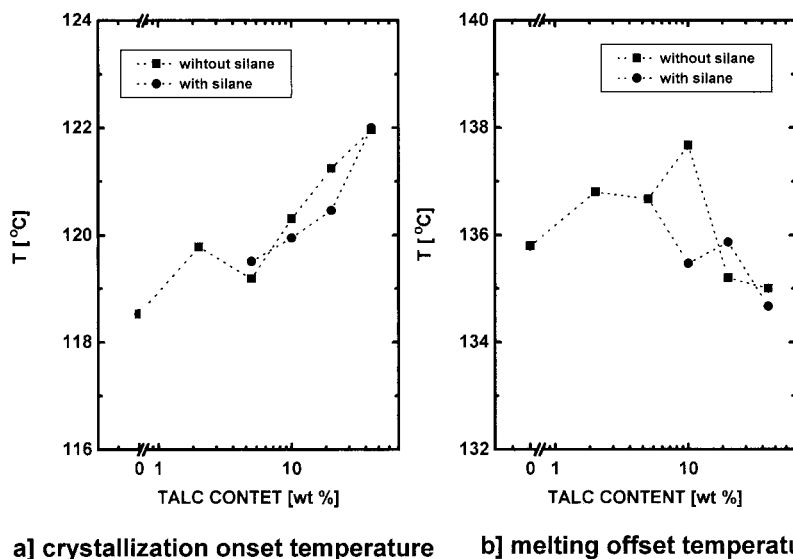


Figure 7 Crystallization and melting temperature of HDPE-talc blends.

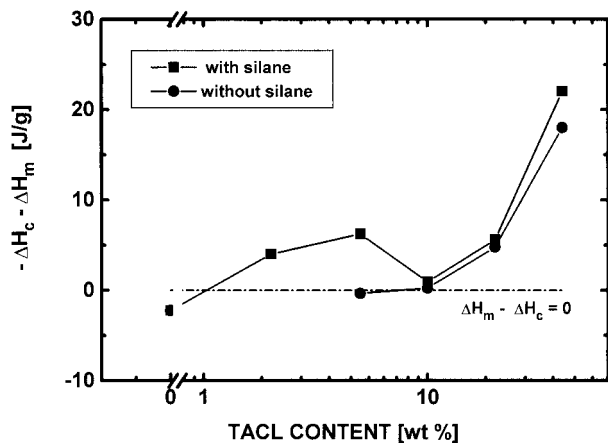


Figure 8 The difference between melting and crystallization enthalpy.

containing system suggests that the additive tends to compensate the loss in chain mobility caused by talcum. Notice that the difference between $(-\Delta H_c - \Delta H_m)$ of silane-containing system and that of the system without it tended to increase with the increase in talc content, and the net silane content had changed with the same trend; the result indicates that silane must have either formed some lubricating layers at polyethylene–talc interface or must have been in matrix to quite an extent. Now that the DSC experiments had been quasi-static ones, in which large-scale flow of polymers cannot be expected, the latter mechanism must have been a dominating one. Diffusion of the additive from the filler surface into the matrix during processing, therefore, should have been important to the succeeding crystallization processes, which, in turn, decides the matrix properties in the filled system.

Analyses Through a Constituent Reinforcing Volume Concept

Although the effects of silane have been proven in the previous sections to be through changing filler dispersion and matrix morphology, besides possibly resulting in certain interfacial structures, contributions from each of these factors cannot be distinguished with ease. The difficulty, however, could be overcome by using percolation analyses founded on a representative reinforcing volume (RRV) concept (Appendix). Owing to the advantage of the percolation theory in treating the transition from short-range interaction to long-range ones in the disordered structures, un-

certainly about filler dispersion encountered in classical treatments⁸ can be circumvented by using theoretical results, which are already available for particulate-filled polymers.¹¹ Analyses of the percolation characteristics of the RRVs yield different dependencies of macroscopic properties on talc content in systems with silane and without, although the current data is not extensive enough to reveal absolute values of percolation thresholds and exponents of the reinforcing units.

Assuming a critical volume fraction V_f^* of 0.00428, which corresponds to an average aspect ratio of 200, curve-fitting of the limited experimental data can yield scaling exponents, τ and γ , of modulus and impact strength, respectively. From Figures 9 and 10, it can be found that the values of τ and γ are larger in the system with silane than in the ones without it, provided that the transition from isolated reinforcing units to percolated networks can be taken as in the range of talcum contents from 1.8 to 7.8 vol % (i.e., 2 to 10 wt %). In agreement with the upper-bound fit (Fig. 1), the higher τ suggests that inclusion of the coupling agent results in better interaction between the reinforcing flakes in the tensile tests. In another words, the effects of silane on the stiffness of the filled plastics had, at least to some extent, been promoting better filler dispersion. By fixing the exponent τ , one would only find lower V_f^* , and thus larger phenomenological aspect ratio A , for systems with silane. Because the aspect ratio here is a measure of talcum particles along with the restricted polymer chains, the increase in A indicates that properties of the average RRV approaches those of individual talc flakes, probably with problem of filler aggregation alleviated

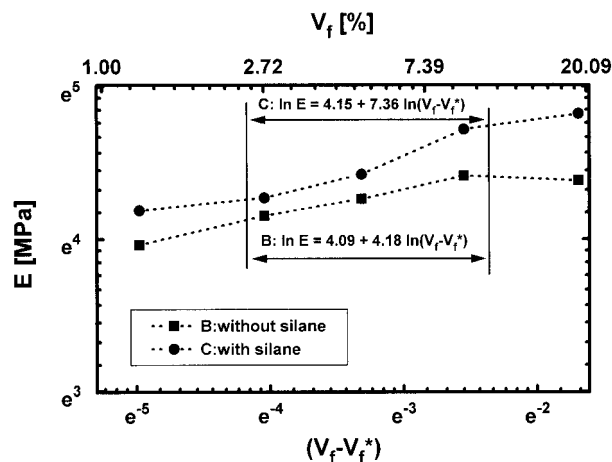


Figure 9 Modulus percolation of HDPE–talc blends.

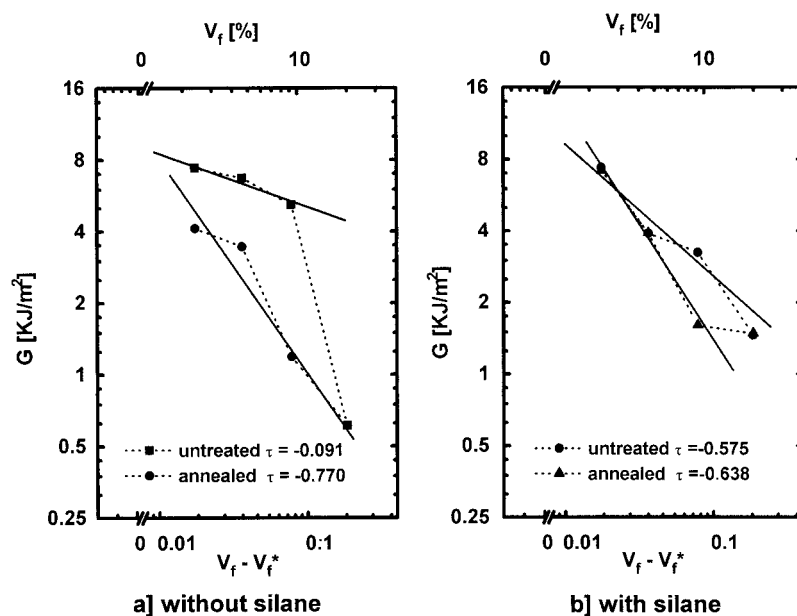


Figure 10 Toughness percolation of HDPE-talc blends.

by the silane. For the same reason, the higher γ , which suggests more rapid decrease of impact toughness with an increase in talc content, reveals a similar trend in filler dispersion.

Comparison of impact toughness of as-processed blends with that of the annealed one would further reveal the effects of silane in promoting filler dispersion and modifying matrix morphology. It can be found from Figure 10 that the treatment results in losses of toughness in blends either with or without silane. Although the model is obviously less suitable for correlating toughness with talc content than in the case of modulus (Fig. 9), a smaller change in the slope of $\ln G$ vs. $\ln(V_f - V_{f^*})$ through the heat treatment could be found in the blends with the additive. Notice that the nonlinearity in Figure 10 means changing RRV with talc content, suggesting the absence of interphase with any well-defined boundary in these filled plastics; the smaller magnitude of the change in slope found in silane-containing blends can only originate from effect of silane on filler dispersion and matrix morphology. The presence of silane in the matrix tends to prevent crystallites from perfection besides accelerating crystallization during cooling stage of processing, resulting in matrix morphology that cannot change much in the heat treatment.

In fact, although higher toughness can always be found in blends of HDPE with silane-treated talc after the heat treatment, it is not the case for the as-processed systems. The toughness had

been highly dependent on talc content before annealing. It had been shown that the effects of the additive on matrix morphology are different when talc content is different. The effects of silane on impact toughness may thus be either positive or negative [as shown in Fig. 2(b)], depending on changes in matrix morphology if there is no large variation in filler dispersion. At low filler contents, silane acted as a certain interfacial barrier to prevent talc from nucleating the crystallization of matrix, making the matrix tougher than the blends with the same content of talc. At higher talc contents, silane that had diffused into the matrix during processing was able to improve chain mobility, besides making crystallites less perfect, as in the neat polyethylene. If the increase in chain mobility had dominated the formation of the morphology of matrix and, thus, made it more brittle, the toughness of coupled HDPE-talc would be lower than that of the filled plastics without it, as shown in Figure 2(b). At the highest talc content of 0.18% (40% by weight), the other aspects of silane's effects on matrix morphology, probably along with changes in filler dispersion, made the blend containing silane tougher than that without it again. The complicated changes in toughness resulting from the presence of silane, therefore, reveal that the effects of silane on the filled plastics can be through enhancing the filler dispersion and modifying matrix toughness, which depends highly on morphology. Its interfacial role, had there been any, is, to a

large extent, to prevent the matrix from forming brittle structure during processing.

In one word, although analyses here had been based on too few experimental data to reach any quantitative RRV parameters, the preliminary results in combination with morphology studies suggest that the effects of the coupling agent are not necessarily all interfacial. Extensive work, therefore, remains to be done for a proper understanding of silane's effects on properties of the filled plastics. Quantitative study of percolation properties of RRV at each narrower range of talc contents is one of methods for the purpose.

CONCLUSION

Through careful analyses of morphology and properties, the following conclusions can be drawn for the present HDPE-talc blends.

1. Treating talc with silane mainly results in higher tensile modulus.
2. Inclusion of silane in neat polyethylene raises the impact strength of the polymer through facilitating its crystallization while hindering the overgrowth of the crystallites.
3. The effects of silane on the matrix morphology vary with talc content: at lower filler contents, it prevents talc from acting as nucleating agents; while at higher talc contents, the additive compensates for the loss in polymer mobility originating from the presence of the filler.
4. Analyses of the dependencies of properties on talc contents reveal that the increase in tensile modulus and complicated changes in impact strength by treating talc with silane may most likely be attributed to changes in filler dispersion and matrix properties.

These results, in combination, suggest that the silane, at least in the present case, enhances dispersion of fillers and modifies the crystalline morphology of matrix, rather than merely resulting in better interfacial structure. It is thus emphasized here that the effects of traditional coupling agents on filler dispersion and matrix morphology are still to be studied further for optimization of filled thermoplastics.

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APPENDIX

Correlation of Properties with Filler Content Through a Modified Percolation Analyses

For a thermoplastic polymer reinforced by flake-like fillers such as talc and mica, enhancement in modulus must originate from the modulus of the filler while that in strength should also be related to change in fracture mechanism. In small deformation, the constituent relationship is no doubt decided by elastic properties of matrix, filler, and interphase, and, most importantly, filler dispersion.⁹ Exact dependency of the modulus on filler content is not always easy to be made for practical systems because the change in filler content usually results in a variation of interfacial properties and filler dispersion. Because the main character of filler dispersion in many filled plastics is that filler forms disordered array, assumptions of super lattice of filler particles⁹ have to be abandoned for treating such problems. The percolation model, a physical simplification in dealing with interaction in disordered structures,¹² is therefore believed suitable. In fact, the method has been proven qualified in describing dependencies of the electrical conductivity on carbon content in conductive plastics,¹³ of the modulus on composition in plastics-rubber blends,¹⁴ and of the impact strength on the rubber component in toughened plastics.¹⁵ The method also is promising in study of phase inversion phenomena in polymer blends.¹⁶ Success in these cases originated from the fact that the dependence of these properties on contents directly correlates with the percolation of the dispersed phase. Because interphasial and interfacial structure rely also on filler contents in the filled plastics considered here, the percolating phase must be considered as consisting of an interphase besides the filler.

Suppose that an average representative reinforcing volume (RRV) consists of one filler particle of average characters, dependency of a macroscopic property of the filled plastics on the filler content can then be defined by percolation of the RRVs, that is,

$$P \sim (V_f - V_f^*)^\delta \quad (\text{A.1})$$

where P stands for the macroscopic property, V_f is the volume content of the filler, δ is the critical exponent, and V_f^* is the percolation threshold, respectively.

In the case of modulus, eq. (A.1) can be rewritten as

$$E = E_0(V_f - V_f^*)^\gamma \quad (\text{A.2})$$

in which E_0 is the modulus of the RRV, and γ is the scaling exponent. The higher the E_0 , the stiffer the RRV will be; the larger the γ , the more profound the increase in filler content affects the plastics property. From the definition of RRV, it can be seen that the larger value of E_0 means a stiffer interphase in the deformation. Percolation threshold V_f^* , on the other hand, has been proved in Kortschot and Woodhams,¹¹ depending on the aspect ratio A of the flake in the theoretical case of rectangular fillers through

$$V_f^* = \alpha/(\beta + A) \quad (\text{A.3})$$

where α and β are constants for a certain set of percolating structure. It is thus quite clear that the A value obtained for the modulus must be a characterization of heterogeneity of RRV. In other words, the higher is its value, the more inhomogeneous the local stress field around the filler would have been. In the case of impact strength, a similar relationship holds, as follows:

$$G = G_0(V_f - V_f^*)^\tau \quad (\text{A.4})$$

where G is the impact strength, G_0 is that of RRV, and τ is the critical exponent. While G_0 and τ have similar meanings compared to E_0 and γ for the effects of filler content on the property, V_f^* , here, does not. Besides elastic fracture work, G

includes, to much extent, the work dissipated in crack initiation and growth during the test. V_f^* , therefore, characterizes the inhomogeneity of microcracking or crazing near the filler surface and, also, possible delamination of the flake-like fillers.

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