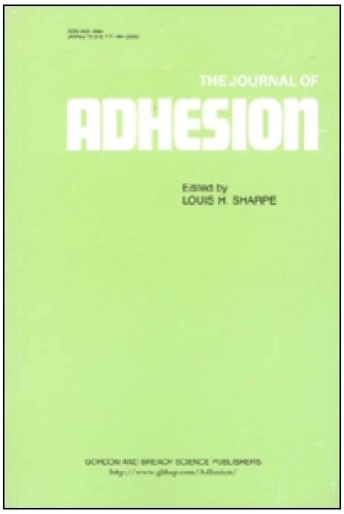

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The Influence of Surface Energetics of Calcium Carbonate Minerals on Mineral-Polymer Interaction in Polyolefin Composites*

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Surface energetics of ground calcium carbonates (GCC), with or without stearic acid treatment, were determined by Inverse Gas Chromatography (IGC). The surface energy data were utilized as a predictive tool to explain the optimum coating level often needed on calcium carbonate minerals to obtain the desirable mechanical strength in filled polypropylene composites. The dispersive components of the surface energies for the uncoated carbonates were also correlated with the corresponding impact resistance data. The surface with the highest energy was found to be the least resistant while the least energetic mineral, on a comparative scale, was the most resistant to impact. It is suggested that understanding the surface energetics of finely-divided solids may be a key for the development of future mineral-filled polymer composites.

Keywords: Inverse gas chromatography (IGC); calcium carbonate minerals; surface energy; adhesion; filled polypropylene (PP) composites; impact strength

INTRODUCTION

Ground and precipitated calcium carbonates are widely used as performance minerals in the rubber, plastics and paper industries. Both

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untreated and surface-modified forms are used, depending upon the nature of the end product [1–3]. In polymer applications the calcium carbonate is often blended with polypropylene (PP) homopolymer or polyethylene (PE) to improve processability and properties such as stiffness and impact resistance of composite materials. For effective mixing and good adhesion characteristics it is desirable that the surface energies of the mineral and polymer are close to each other [4].

Adhesion is a thermodynamic event and it depends not only on the dispersion force interactions but also on the acid-base interactions of the two interacting bodies [5, 6]. In some cases, enhancement of this event is required (*e.g.* in surface modification of minerals) while in others there is a thermodynamic need to decrease this for obtaining optimum properties such as decrease in brittleness and increased impact resistance of the mineral-filled composites. Therefore, a knowledge of the surface energetics of the two interacting bodies is important.

In this work, Inverse Gas Chromatography (IGC) has been used to obtain information about the surface energetics and acid/base properties of untreated and surface-modified ground calcium carbonates. IGC is a powerful technique which has been applied in recent times to obtain such information on solid surfaces. It is gaining increasing popularity because of its sensivity, speed, accuracy and simplicity. It is particularly useful in the linear regime of the adsorption isotherm (Henry's Law region) where the adsorption is a linear function of the adsorbate concentration [7, 8]. The theoretical basis and instrumentation of the IGC technique is the same as that of analytical GC. The only difference being that in IGC one is interested in the surface properties of the finely-divided solid (the stationary phase) packed in the column. Organic molecules of known chemical structures are injected into the column, along with the carrier gas stream, at infinite dilution and their retention parameters are measured by using standard methods [9]. The most widely used retention parameter is the specific retention volume of the probe molecules which is related to almost all the thermodynamic parameters of the gas-solid interactions. The specific retention volume is used to obtain the isosteric heats of adsorption and the components of the surface energies, both dispersive and polar, of the adsorbent. In this report, the surface energies of various ground calcium carbonates were correlated with the impact resistance data of PP filled with these minerals and their influence, on the properties of final composites, were recognized.

IGC THEORY AND EXPERIMENTAL

Specific or net retention times or volumes of gaseous probe molecules eluted through a chromatographic column packed with a powdered material of interest are related to almost all the thermodynamic parameters describing gas/solid adsorption equilibria [10]. The specific retention volume, Vg, is related to the standard adsorption energy by the following relationship.

$$\Delta G_a = -RT \ln Vg + C \tag{1}$$

where $Vg = V_n(273)/T.w$ and since the mass of the adsorbent, w, is constant the net retention volume, V_n, may be utilized for the above calculation. $V_n = V_r - V_0$ where V_r is the retention volume of the probe under study and V_0 is the retention volume of a non-sorbed species (usually methane) by the adsorbent. The constant, C, is dependent on the reference state of the probe [7]. The (equilibrium) surface energy of solids has the same meaning as that of the surface tension of liquids. Owing to the flexible nature of the liquid interfaces, it is easy to measure their surface tensions but due to the rigid nature of solids we need an indirect method to assess their surface tension values. Static gas adsorption methods are useful for this purpose but they are time consuming and can be cumbersome. In utilizing IGC as a measurement tool, Dorris and Gray have related the incremental free energy of adsorption, ΔG_{CH_2}, by the following empirical relationship in order to obtain the dispersive component of the surface energy [11].

$$\Delta G_{CH_2} = -RT \ln(V_N^{Cn+1}/V_N^{Cn}) \tag{2}$$

$$\gamma_S^D = (-\Delta G_{CH_2}/2.Na_{CH_2})^2 (1/\gamma_{CH_2}) \tag{3}$$

V_N^{Cn+1} and V_N^{Cn} are the net retention volumes of two successive alkanes having C_n and C_{n+1} carbon numbers. γ_S^D is the dispersive component of the surface free energy in mJ/m^2, N is Avogadro's constant, R is the universal gas constant, a_{CH_2} is the area of a $—CH_2$ group (0.06 nm^2) and γ_{CH_2} is the surface free energy of a surface constituted with $—CH_2$ groups, *e.g.* polyethylene, and is also temperature dependent; $\gamma_{CH_2} = 35.6 + 0.058(293 - T)$ where T is in °K and γ_{CH_2} in mJ/m^2. The polar interaction potential, especially the acidity of the surface, may also be estimated from the following relationship.

$$\Delta G_{\text{acid}} = -RT\,[\ln V_{n(\text{alkene})} - \ln V_{n(\text{alkane})}] \tag{4}$$

Since the cationic sites on the calcium carbonate surface are electron acceptors, these will attract the π-electrons of the alkene molecules and the acid interaction potential of the surface can be estimated by applying the Eq. (4) [28]. Following a similar strategy, a number of years ago, one of us demonstrated that the specific interaction energy of precipitated calcium carbonate was greatly affected by various treatments given to its surface [14].

The experimental details and the necessary precautions for studying the calcium carbonate surfaces by IGC have been described by one of us in previous publication [9]. Stainless steel columns, of 6mm o.d. and lengths ranging from 40–60 cm, were packed with 10–12g of 250–450 μm aggregated ground calcium carbonates. The columns were fitted into a Hewlett Packard Model 5890 Gas Chromatograph equipped with a flame ionization detector. The flow rate of the carrier gas (helium) was adjusted to 20–25 ml/min and was corrected for the pressure drop across the column. Vapor samples of the hydrocarbon probes were introduced into the carrier gas stream by a Hamilton gas-tight 100 μl syringe. The hydrocarbons were of high purity (better than 99%) and gave a single peak in the chromatograms. Triplicate injections were made and the net retention volumes were reproducible to within 1%. The columns were conditioned at 100 and 150°C for the set of data shown in Figures 1 and 3, respectively. Retention times of various alkanes such as hexane, heptane and octane were measured at 80°C. The reported surface energies were derived by using Eqs. (2) and (3). The reproducibility was within 1–2 mJ/m^2.

The compounding of polypropylene was done on an APV MP2030 co-rotating twin screw compounder with temperature profile of 210 (die), 205, 200, 190, 180, and 155°C. Plaques were moulded on an Arburg 320-750-210 injection moulding machine. The temperature profile across the barrel was 230 (nozzle), 225, 210, 200°C. The moulded temperature was 60°C. All the moulded specimens were stored at controlled temperature (20°C) for 5 days before impact strength tests. The instrumented falling weight impact strength (IFWIS) were recorded on

80 mm × 80 mm × 2 mm plaques using a Rosand Falling Weight Impact Tester Type 5 at 20°C. The impact speed was 4.4 m/s and the mass associated with the tup was 25 Kg. The data are an average of 8 tests with the variation of 2 J/mm and 0.40 – 1.20 J/mm for Figures 2 and 3, respectively.

RESULTS AND DISCUSSION

Untreated and stearic-acid-treated ground calcium carbonate minerals were analysed for their surface energies. The specimen used in stearic acid coating experiments (Figs. 1 and 2) was a 1.3 μm ground calcium carbonate. The three uncoated materials (Fig. 3) shared similar physical characteristics (mean particle size of 3 μm) but originated from different sources/processes. Figure 1 shows the dispersive surface energy change brought about by various dosages of stearic acid on the

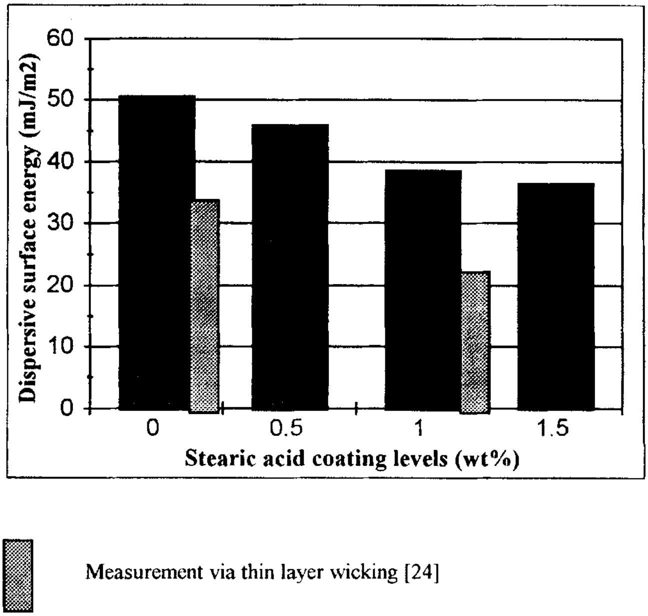

FIGURE 1 Variation of dispersive surface energies of ground calcium carbonates with stearic acid coating levels.

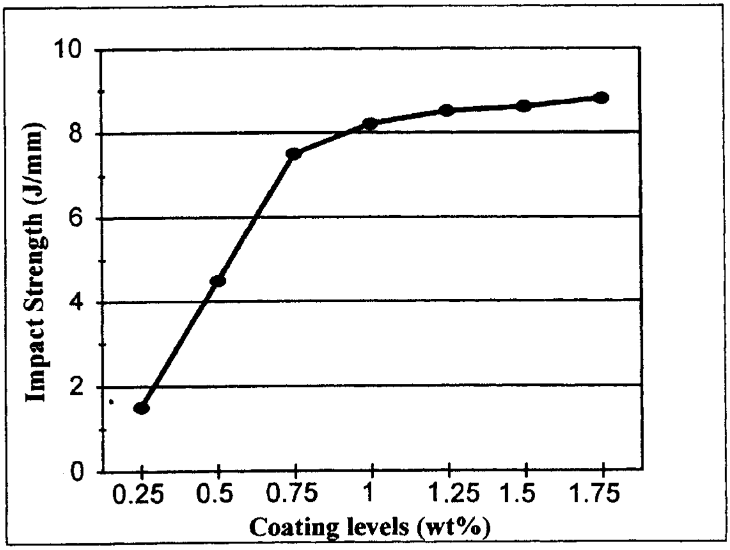

FIGURE 2 Effect of stearic acid coating levels on the impact strength of calcium-carbonate-filled polypropylene homopolymer.

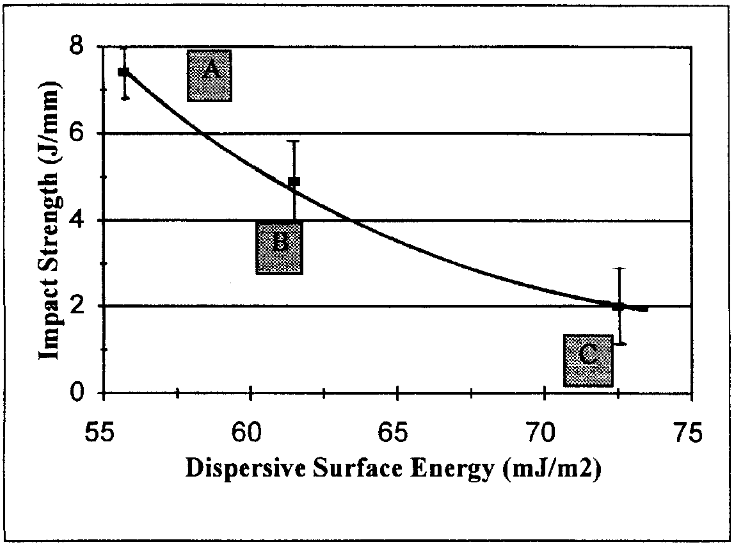

FIGURE 3 Variation of impact strength of filled PP homopolymer with dispersive surface energies of the uncoated carbonates.

calcium carbonate. Few changes were observed after 1 wt% coating level. Adopting the procedure of Papirer *et al.* [15] and assuming the cross sectional area of the stearic acid molecule as being 21 A^2, 1 g of stearic acid would cover around 445 m^2 of the available mineral surface. The BET-nitrogen surface area of coated carbonates used in this study ranged from 4–5 m^2/g which would ensure about 90–100% surface coverage by 1 wt% stearic acid treatment. The polar interaction potentials are not reported here since the dispersion force interaction is of prime importance as far as interfacial wetting of polypropylene and mineral is concerned. In fact, it is necessary that the polarity of the surface is reduced to a bare minimum or completely eliminated to avoid compounding and water adsorption problems [16]. Figure 2 correlates this information with the impact resistance data obtained with various loadings of the fatty acid. The impact resistance approaches a plateau at about 1 wt% stearic acid coating level and, thereafter, no significant changes are observed. A surface constituted of close-packed CH_2 groups has a surface energy of about 32–35 mJ/m^2 at temperatures ranging from 80–20°C, respectively [11, 15, 17]. Individual polypropylene products might have slight variation from this general classification [18]. Therefore, if the coated minerals have surface energies closer to this value, as was observed in the present case, one would expect reasonable adhesional and dispersion properties with the polymeric matrix. A reduced interfacial adhesion between the hydrophobic calcium carbonate particles and polypropylene is necessary for better dispersion of the mineral particles in the polymer matrix, leading to better and more efficient dissipation of impact energy [19]. Accordingly, the data presented in Figure 1 and 2 are generally in good agreement with each other.

Papirer *et al.* have also studied the effect of stearic acid treatment on precipitated calcium carbonates and showed that at about 75% coverage the surface energy is minimized to a significant level and that further treatments brought about little change to the surface energies [15]. There is also some evidence in the literature that even a coverage less than the monolayer may be sufficient to obtain the desired strength properties in polyolefin-based composites and that it is difficult to analyse the coverage even by using a variety of surface analytical techniques [20]. This is not surprising given the fact that the calcium carbonate surface, like many finely-divided solids, is heterogeneous in nature and the surface coverage can hardly be predicted with full confidence. Significant response to the stearic acid treatment would be by high energy cationic sites on the surface [9, 14, 20].

It is, however, surprising that the uncoated carbonates also follow a similar trend despite the fact that the surface energies of these specimens were not close to that of polypropylene. However, it must be pointed out that the impact properties of composites filled with these carbonates were significantly lower than those typically observed with stearic-acid-treated carbonates. Some of this reduction in impact strength was due to a higher concentration of coarse ($>20\,\mu$m) particles. An inverse relationship in Figure 3. between the surface energies and the corresponding impact data shows that the surface energies of these carbonates were playing an important role in determining the end product property. The particle size distribution and the BET surface areas of these uncoated carbonates were similar to each other but, in spite of good dispersion in the polypropylene matrix (observed by scanning electron microscopy), the variation in their impact properties was difficult to understand until we started doing the appropriate surface analysis. The corresponding surface energy differences shown in Figure 3 may arise due to a variety of reasons including the methods used to process ground carbonates in an industrial environment.

One of the challenges faced by industrial adhesion scientists and engineers is to relate the fundamental thermodynamic properties of surfaces to the end product properties. These may include materials ranging from powdered surfaces to "flat" surfaces such as self-assembled monolayers on solid substrates for a variety of applications [21, 22]. Although the latter could be studied *via* contact angle methods utilizing the reasonably well established theories of van Oss, Good and Chaudhury [23], powdered surfaces are difficult to study by this method. To illustrate this fact we carried out a few experiments to measure the surface energies of uncoated and coated calcium carbonate specimens by a thin layer wicking technique [24] and the corresponding data are presented in Figure 1. It is noteworthy that, although the absolute values are significantly lower, the trends reflect the data derived from IGC experiments. The discrepancy in the scale of the magnitude of the dispersive surface energies obtained by two methods may be understood by considering the surface interaction proceses involved in these methods. The IGC, when applied at infinite dilution, provides information about the high energy sites on a solid surface but when higher volumes of the probe molecules are injected the macroscopic surface energetic picture becomes comparable with the information obtained from the contact angle measurements. For relatively low energy surfaces the expected difference would be around 2–5 mJ/m^2 between the two methods [13]. In view of these observations, it seems likely that the relatively large differences (14–15 mJ/m^2) observed in the present work, especially with coated samples, could also be related to the inherent weaknesses in the theory and practice of the thin layer wicking technique to derive the contact angles of the corresponding liquids on powdered surfaces [25–29]. A vast number of papers regarding the application of IGC to study the surface chemistry of carbons and carbon fibers [30–39], silicas [40–42] aluminas [43], titanium dioxide [13, 44–46], glass fibers [6], cellulose fibers [47], untreated and surface-modified calcium carbonates [4, 9, 14, 15, 44, 48, 49] have been published but only in few cases were the measured properties correlated with the appropriate product's properties [6, 38, 39, 44, 46, 47, 49].

Although the significance of shape and size distribution of particles has always been recognized in explaining the corresponding differences in the mechanical properties of the mineral-filled composites [50], less attention has been given to the corresponding relationship with the surface properties of the pigments. In this brief report we demonstrated that there is a noticeable relationship between the surface properties of powdered solids and their interaction with compatible polymers such as PP homopolymers which should not be underestimated by mineral producers and end users. It is expected that more industrially-related research work will be done along these lines in the near future.

CONCLUSION

IGC is a convenient tool to obtain information about the surface properties of powdered materials. Surface energetics of powdered material do play a crucial role in their adhesional and dispersion properties when these materials are blended with compatible polymeric materials. A knowledge about the surface properties of untreated and surface-modified minerals is key to the development of high performance materials for tomorrow's composites.

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References

[1] Katz, H. S. and Milewski, J. V., Eds., *Handbook of Fillers and Reinforcement for Plastics* (Van Nostrand-Reinhold, NY, 1978).
[2] Reisch, M. S., *Chem. Eng. News* **69**(17), 9 (1991).
[3] Nakatsuka, T., *Polym. Sci. Technol.* **25**, 51 (1985).
[4] Schreiber, H. P., Viau, J.-M., Fetoui, A. and Denz, Z., *Polym. Eng. Sci.* **30**(5) 263 (1990).
[5] Fowkes, F. M., *Polym. Sci. Technol.* **12A**, 43–52 (1980).
[6] Ulkem, I. and Schreiber, H. P., *Composite Interfaces* **24**, 253 (1994).
[7] Lloyd, D. R., Schreiber, H. P. and Ward, T. C., Eds., *Inverse Gas Chromatography ACS Symposium Series* (American Chemical Society, Washington, DC, 1989), **391**.
[8] Balard, H. and Papirer, E., *Prog. Org. Coatings* **22**, 1–17 (1993).
[9] Ahsan, T., Colenutt, B. A. and Sing, K. S. W., *J. Chromatogr.* **464**, 416 (1989).
[10] Conder, J. R. and Young, C. L., *Physicochemical Measurement by Gas Chromatography* (John Wiley, New York, 1979).
[11] Dorris, G. M. and Gray, D. G., *J. Colloid Interface Sci.* **77**, 353 (1980).
[12] Saint-Flour, C. and Papirer, E., *Ind. Eng. Chem. (Prod. Res. Dev.)* **21**, 666 (1982).
[13] Fafard, M., EL-Kindi, M., Shreiber, H. P., Dipaola-Baranyi, G. and Hor, A. M., *J. Adh. Sci. Technol.* **8**, 1383 (1994).
[14] Ahsan, T., Colenutt, B. A. and Sing, K. S. W., *J. Chromatogr.* **479**, 17 (1989).
[15] Papirer, E., Schultz, J. and Turchi, C., *Eur. Polym. J.* **20**, 1155 (1984).
[16] Rothon, R. N., *Eur. Rubber J.* **166**, 37 (1984).
[17] Aveyard, R., *J. Colloid Interface Sci.* **52**, 621 (1975).
[18] Lee, L.-H., *Polym preprints, Div. Polym. Chem.* (ACS meeting, Orlando, Florida, 1996), **37**, 97–98.
[19] Jancar, J., Dibenedetto, A. T. and Dianselmo, A., *Polym. Eng. Sci.* **33**, 559 (1993).
[20] Fekete, E., Pukanszky, B., Toth, A. and Bertoti, I., *J. Colloid Interface Sci.* **135**, 200 (1990).
[21] Gorman, C. B., Biebuyck, H. A. and Whitesides, G. M., *Langmuir* **11**, 2242 (1995).
[22] Uiman, A., *An Introduction to Ultra Thin Organic Films from Langmuir-Blogett to Self Assembly* (Academic Press, San Diego, 1991).
[23] van Oss, C. J., Chaudhury, M. K. and Good, R. J., *Chem. Rev.* **88**, 927 (1988).
[24] Giese, R. F., Costanzo, P. M. and van Oss, C. J., *J. Phys. Chem. Miner.* **17**, 611 (1991).
[25] Heetjes, P. M. and Kossen, N. W. F., *Powder Technol.* **1**, 33 (1967).
[26] Buckton, G., *J. Adh. Sci. Technol.* **7**, 205 (1993).
[27] Good, R. J. and Lin, N. J., *J. Colloid Interface Sci.* **54**, 52 (1976).
[28] Good, R. J., *J. Colloid Interface Sci.* **42**, 473 (1973).
[29] Costanzo, P. M., Wu, W., Giese, Jr., R. F. and van Oss, C. J., *Langmuir* **11**, 1827 (1995), and references therein.
[30] Nardin, M., Balard, H. and Papirer, E., *Carbon* **28**, 48 (1990).
[31] Jagiello, J., Bandoz, T. J. and Schwarz, J. A., *Carbon* **30**, 63 (1992).
[32] Jagiello, J., Bandoz, T. J. and Schwarz, J. A., *Colloid Interface Sci.* **151**, 433 (1992).
[33] Vukov, A. J. and Gray, D. G., *Langmuir* **4**, 743 (1988).
[34] Dong, S., Brendle, M. and Donnet, J.-B., *Chromatographia* **28**, 469 (1989).

[35] Qin, R.-Y and Donnet, J.-B., *Carbon* **32**, 165 (1994).

[36] Wang, M.-J., Wolff, S. and Donnet, J.-B., *Rubber Chem. Technol.* **64**, 559 (1991).

[37] Wang, M.-J., Wolff, S. and Donnet, J.-B., *Rubber Chem. Technol.* **64**, 714 (1991).

[38] Ayala, J. A., Hess, W. M., Joyce, G. A. and Kistler, F. D., *Rubber Chem. Technol.* **66**, 772, (1993).

[39] Ayala, J. A., Kistler, F. D. and Joyce, G. A., *Rubber Chem. Technol.* **64**, 19 (1991).

[40] Ligner, G., Vidal, A., Balard, H. and Papirer, E., *J. Colloid Interface Sci.* **133**, 200 (1989).

[41] Jagiello, J., Ligner, G. and Papirer, E., *J. Colloid Interface Sci.* **137**, 128 (1990).

[42] Papirer, E., Balard, H. and Sidqi, M., *J. Colloid Interface Sci.* **159**, 238 (1993).

[43] Papirer, E., Perrin, J.-M., Siffert, B. and Philipponneau, G., *J. Colloid Interface Sci.* **144**, 263 (1991).

[44] Dong, S., Schreiber, H. P. and Haber, A., *ANTEC* **30**, (1991).

[45] Hegedus, C. R. and Kamel, I., *J. Coating Technol.* **65**(820), 31 (1993).

[46] Malik, T. M., Carreau, P. J., Schreiber, H. P., Rudin, A., Kale, L. and Tchir, W., *J. App. Polym. Sci.* **43**, 543 (1991).

[47] Felix, J., Galenholm, P. and Schreiber, H. P., *J. App. Polym. Sci.* **51**, 285 (1994).

[48] Kellers, S. and Lunar, P., *Tappi Proceedings, Coating Conference* 349 (1992).

[49] Ulkem, I., Bataille, P. and Schreiber, H. P., *J. Macromol. Sci.-Pure App. Chem.* **A31**(3) 291 (1994).

[50] Riley, A. M., Paynter, C. D., McGenity, P. M. and Adams, J. M., *Plastics & Rubber Processing and Applications* **14**, 85 (1990).