Optical Properties of Particle-Filled Polycarbonate, Polystyrene, and Poly(methyl methacrylate) Composites

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ABSTRACT: Transparency is a key material property of polycarbonate (PC), polystyrene (PS), and poly(methyl methacrylate) (PMMA). To study the optical properties of particle-filled PC, PS, and PMMA, composites containing inorganic particles in different sizes and concentrations were produced by direct melt mixing in this work. The optical properties characterized by total light transmittance, haze, and clarity were studied. The results show that the optical properties of polymer composites are strongly affected by particle content, particle size, and especially by difference in refractive indices between polymer matrix and particles. It is also revealed that the light transmittance and haze of composites are mainly affected by difference in refractive indices, whereas the clarity is more affected by particle size. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 1866–1872, 2010

Key words: transparency; composites; polycarbonate; polystyrene; poly(methyl methacrylate)

INTRODUCTION

In recent years, optically transparent polymer composites have been the subject of many investigations because of their novel properties and industrial applications, such as optical fiber sensors, optical isolators, packaging products, and medical devices.[1–4] According to ASTM D 1003 standard, the transparency of plastic materials is characterized by light transmittance, haze, and clarity. Haze is the degree to which the specimen reduces the apparent contrast of the object. This aspect of transparency is commonly referred to as loss of contrast. The last parameter of transparency describes the degree to which fine details may be resolved in the object. This ability of a specimen is known as see-through quality. It is known that these parameters are independent to each other and it is possible for a sample, which haze value is deteriorating whereas its clarity is improving.[5] An amorphous thermoplastic material is transparent without containing fillers causing transparency loss. However, polymer composites become hazy by incorporation of fillers. It is reported that the major factor of loss of transparency is light scattering loss because of the fluctuation of refractive index caused by density fluctuation.[6] Besides difference in refractive indices between polymer matrix and filler, some other parameters also influence the composite transparency, such as filler concentration, particle size, and dispersion quality of particles.[7] Techniques for achieving transparent polymer composites include *in situ* polymerization, using surfactants, emulsion/miniemulsion techniques, and direct melt compounding.[8–13]

Transparency is a key property of polycarbonate (PC), polystyrene (PS), and poly(methyl methacrylate) (PMMA), which are all amorphous thermoplastics and often used as an alternative to glass. For example, PC has been used in the medical market regarding its transparency and unique mechanical properties, such as filter housings, tubing connectors, and surgical staplers.[14] It is known that incorporation of nanoparticles into these plastic materials can achieve some improvements in mechanical and/or thermal properties.[15–17] Besides improvements in mechanical and thermal properties, it is also important to maintain the transparency of these materials for many desired applications. Compared with inorganic glass, transparent reinforced polymer composites have some advantages such as much lighter in weight and higher impact strength.

Our main goal in this study is to characterize the optical properties of reinforced PC, PS, and PMMA. For that purpose, nanosilica (SiO_2) was used as main filler. To evaluate the influence of particle size on composite transparency, microparticle alumina (Al_2O_3) was used as an alternative to nanosilica for

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PS, because it was reported that the incorporation of alumina microparticles into PS significantly improved the mechanical properties of matrix.[18] All composites were produced by direct melt compounding in a laboratory kneading machine and then compression molded. It was expected that the shear forces by melt compounding should be helpful to support the dispersion and deagglomeration of the fillers. This study was focused on the evaluation of transparency of composites produced; the characterization of mechanical properties will be presented in another work.

EXPERIMENTAL

Materials

Granulated bisphenol-A PC (Makrolon 3105 of Bayer AG, Germany), PS (Polystyrol 158 K of BASF, Germany), and PMMA (TEREZ 5005 of TER HELL PLASTIC, Germany) were used as polymeric matrices in this work. The refractive indices at 589 nm light wavelength of PC, PS, and PMMA are 1.58, 1.59, and 1.49, respectively. The molecular structures of these polymers are given in Figure 1. The fumed nanoparticle SiO_2 (Aerosil R106 of Evonik, Germany) and microparticle Al_2O_3 (Disperal 11N7-80 of Sasol GmbH, Germany) were used as fillers. The nanosilica was surface-modified to be hydrophobic before supplying. The boehmite alumina had a hydrophilic nature without chemical treatment. The important characteristics of both particles given by suppliers are listed in Table I. All materials were used as received.

Sample preparation

All raw materials were predried in an oven at 70°C for 12 h before compounding process. The particle powder was added into the respective molten polymer in a kneading machine equipped with counter-rotating screws (Brabender, Germany). The mixture was kneaded at a screw speed of 60 rpm for 6 min. The process temperatures for PC, PS, and PMMA were 270, 170, and 200°C, respectively. The particle concentration in composites was set at 0, 2, 3, and 4 vol %. After compounding process, all samples were prepared by compression molding.

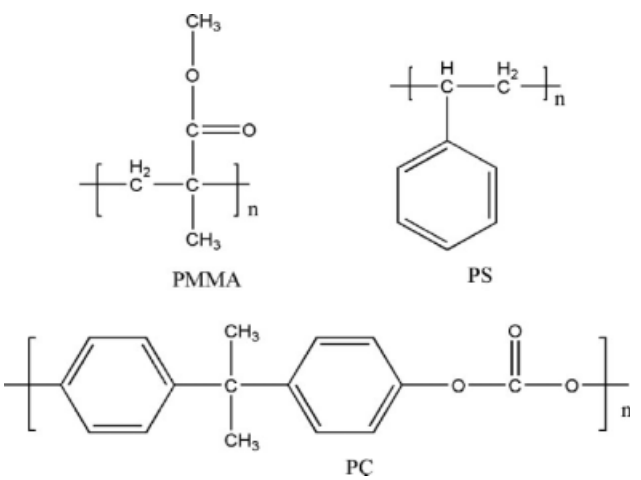

Figure 1 Molecular structures of PC, PS, and PMMA.

TABLE I
Characteristics of Silica and Alumina Particles

Particle characteristics	Particle type	
	Silica	Alumina
Particle content (wt %)	≥99.8 (SiO_2)	=80 (Al_2O_3)
Primary size	7 nm	40 μm
Specific surface area (m^2/g)	250 ± 30	100
Refractive index	1.45	1.66[19]

Characterization of composites

Figure 2 illustrates some dimensionless parameters that are commonly measured to characterize the transparency of materials. A light beam Φ_0 is incident upon a sample, and a diminished undeviated transmitted beam Φ_t emerges on the far side. The forward-scattered light flux denoted by Φ_f may be subdivided into two ranges of scattering angle, namely from 0° to 2.5° ($(\phi_f)_0^{2.5}$) and from 2.5° to 90° ($(\phi_f)_{2.5}^{90}$). Some parameters of transparency are defined as follows:[5]

$$L_D = \frac{\phi_t}{\phi_0} \quad (1)$$

$$L_T = \frac{\phi_t + \phi_f}{\phi_0} \quad (2)$$

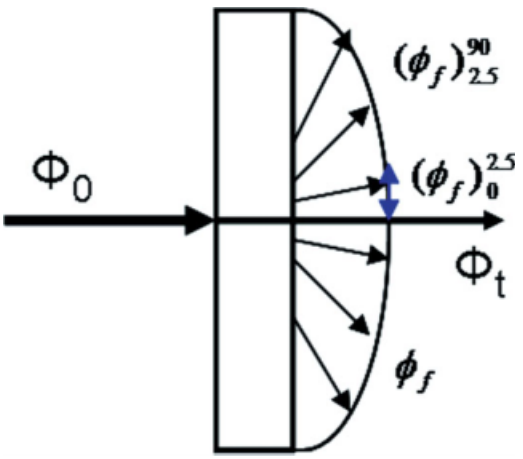

Figure 2 Definition of some parameters used to characterize the transparency of materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$H = \frac{(\phi_f)_{2.5}^{90}}{\phi_t + \phi_f}, \quad (3)$$

where L_D, L_T, and H are the direct light transmittance, the total light transmittance, and the haze, respectively. Different from the test situation for haze and light transmittance, where the standard measurement is widely used and almost universally accepted, there are several methods for characterization of clarity, which differ in principle and detail.[20] A small-angle scattering method was used in this work. Small-angle scattering deflected the light beam in small angles, so that the light intensity was concentrated within this narrow angular range and determined.

In general, light losses mainly due to reflection at the outer surface of samples and at the interfaces between polymeric matrix and particles. This reflection occurs because of the difference in the refractive indices between different media. The reflection coefficient R is given by Fresnel's equation:[21]

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2, \quad (4)$$

where n_1 and n_2 are the refractive indices of polymeric matrix and particles, respectively. Equation (4) indicates that the larger the difference in refractive indices, the more light will be reflected.

The optical characterizations were carried out according to ASTM D 1003 and ASTM D 1044 standards in an instrument (BYK-Gardner GmbH, Germany). The samples used had a dimension of $60 \times 60 \times 2$ mm^3 (length $\times$ width $\times$ thickness). The light wavelength used was 589 nm.

The dispersion quality of particles in matrices was examined by using scanning electron microscopy (SEM, JEOL JSM-6300 and Hitachi S5200). The surface roughness of samples was characterized using white light profilometer (FRT, Germany). To evaluate the possible crystallinity induced by particles in composites, differential scanning calorimetry (DSC) was carried out in a Mettler Toledo instrument under nitrogen atmosphere. A thermogravimetric analysis (TGA) was performed to study the thermal stability and degradation state of materials after kneading process.

RESULTS AND DISCUSSION

Morphology analysis

The SEM picture in Figure 3 shows the free nanoparticles taken from particle powder. It is evident that the nanoparticles agglomerate even in free state because of strong interaction between the particles. The primary particle size is about 40 nm. Figure 4 reveals the surface morphology of PC/SiO_2 composites filled with 2 and 4 vol % particles as well as PS/SiO_2 and PMMA/SiO_2 composites containing 4 vol % particles. It can be seen that the nanoparticles are well homogenized in PS and PMMA matrices with an approximate average size of about 80 nm. In PC composites, the nanoparticles agglomerate in a higher degree than in PS and PMMA, and the number of silica agglomerates increases with increasing particle concentration. The possible explanation is that untreated PS and PMMA are more hydrophobic in surface polarity than bisphenol-A PC (hydrophilic) because of their molecular structures as shown in Figure 1. As PS, PMMA, and nanosilica used have similar surface polarity, the compatibility and dispersability of nanoparticles in PS and PMMA matrices should be better than in PC matrix.

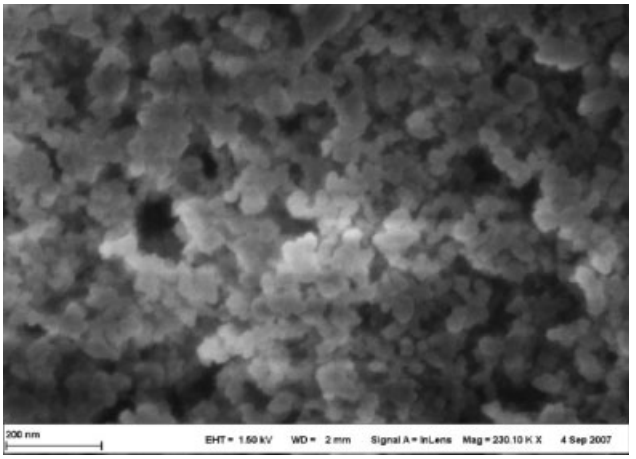

Figure 3 SEM image of free silica nanoparticles taken from particle powder.

Figure 5 shows the dispersion state of microparticles in PS/Al_2O_3 composites filled with 2 and 4 vol % particles, respectively. From the figure, large alumina agglomerates in a micrometric range are observed, and the size of such agglomerates obviously increases with increasing particle concentration. Besides particle concentration, the different chemical nature of PS (hydrophobic) and alumina particles (hydrophilic) should have a negative influence on dispersion quality of microparticles. On the other hand, it is revealed that the shear forces by mixing process were not effective enough to break down such agglomerates. In general, it is difficult to achieve a very good dispersion of microparticles using normal dispersion technique such as direct melt compounding.[18]

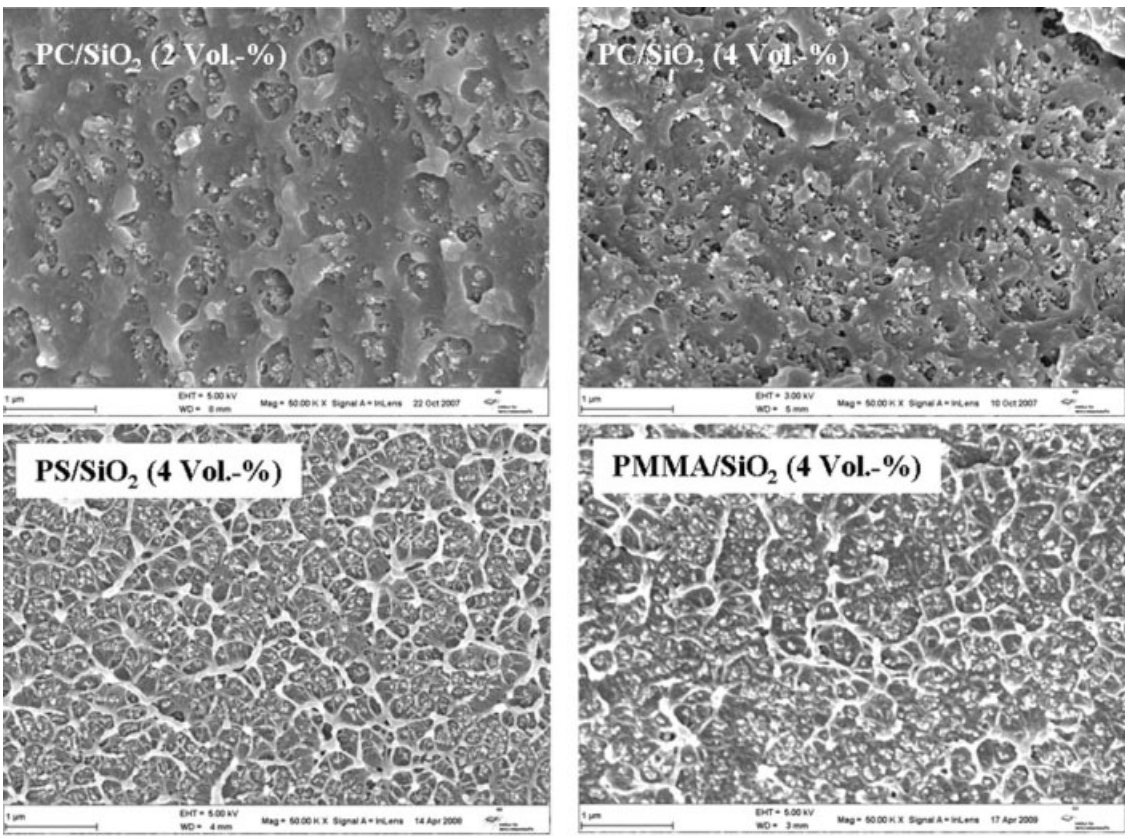

Figure 4 SEM images of PC, PS, and PMMA composites filled with silica particles.

Transparency analysis

One important factor of transparency is the difference in refractive indices between polymer and filler. The differences in refractive indices of PMMA/SiO_2, PS/Al_2O_3, PC/SiO_2, and PS/SiO_2 are 0.04, 0.07, 0.13, and 0.14, respectively.

The outer surfaces of respective samples are smooth with an average surface roughness below 1 μm, indicated by surface analysis in this work. It is known that surface roughness on the 100-μm size range is responsible for a loss in transparency, whereas surface roughness in the submicron range does not affect the transparency.[22] Accordingly, the influence of surface roughness on transparency measurements can be ignored in our study.

In general, the presence of inorganic particles in polymer matrix can increase the crystallinity of matrix because of inhomogeneous nucleation effect and subsequently decrease the transparency of this matrix. However, the DSC analysis indicates that there is no obvious crystallization observed in PC, PS, and PMMA composites. Therefore, an effect of crystallization on transparency can also be neglected.

The total light transmittance of all samples as a function of particle concentration is shown in Figure 6. Obviously, increasing particle concentration leads to a decrease of total light transmittance for all composites because of increasing light reflection at optical interfaces between polymer matrix and particles. At given particle concentration, the value of total light transmittance of composites increases according to the following order: PC/SiO_2 < PS/SiO_2 < PS/Al_2O_3 < PMMA/SiO_2. Independent of particle concentration, PMMA/SiO_2 composites exhibit the highest light transmittance as a result of the smallest difference in refractive indices (0.04). The PMMA/SiO_2 nanocomposites produced in this work are clearly transparent up to 10 vol % SiO_2 at which the total light transmittance is 78.6%. On the contrary, PC/SiO_2 composites show the lowest light transmittance among the composites, although the combination PC/SiO_2 does not have the largest difference in refractive indices (0.13). It is found that PC shows an obvious discoloration after kneading process in Brabender mixer because of possible thermal degradation or hydrolysis of carbonate groups, which are very sensitive to high temperature and hydroxyl groups according to Davis and Golden.[23,24] This consideration is proved by TGA analysis as shown in Figure 7. It can be seen that untreated neat PC is more thermally stable than that after kneading process, indicated by a lower decomposition rate of untreated PC. Obviously, the presence of degradation products (products after rearrangement of

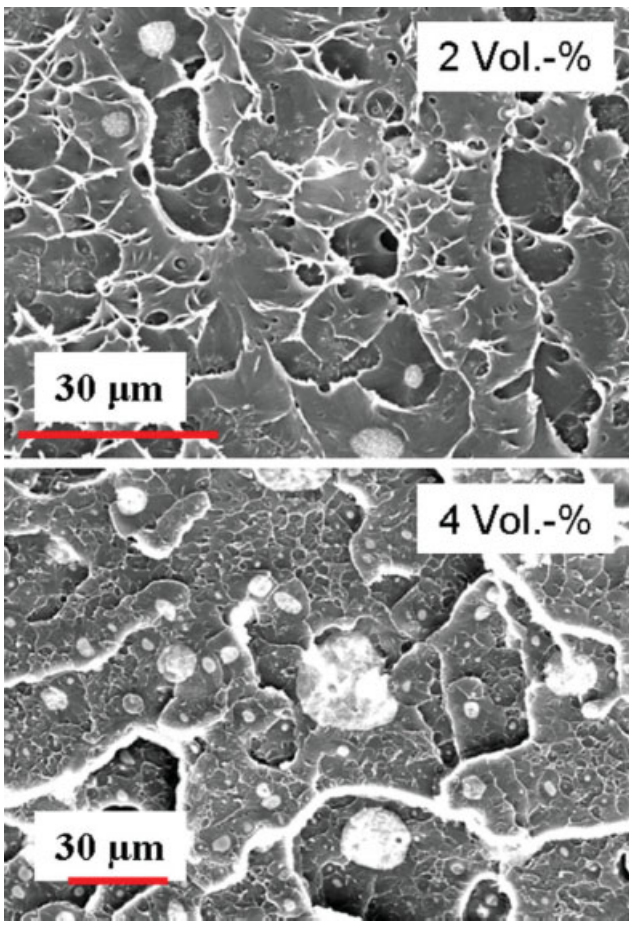

Figure 5 SEM images of PS/Al_2O_3 composites filled with 2 and 4 vol % particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

carbonate groups) in PC causes this decrease of thermal stability and a reduction of transparency. PS/Al_2O_3 composites show higher total light transmittance compared with PS/SiO_2 composites despite

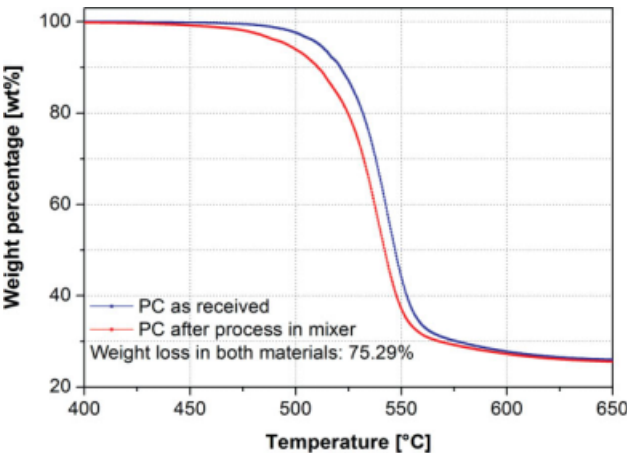

Figure 7 Comparison of thermal stability of neat PC before and after kneading process obtained by TGA analysis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of poor microparticle dispersion, which is a result of smaller difference in refractive indices in case of PS/Al_2O_3 combination. In summary, the result of total light transmittance correlates well with the order of difference in refractive indices of analyzed combinations.

The results of haze measurements are presented in Figure 8. The haze value of all composites increases with increasing particle concentration because of increasing light loss via reflection and scattering. It is noted that the haze value of PMMA composites increases only slightly because of perfect index-matching, whereas the other composites show a drastic increase in haze. From Figure 8, PS/Al_2O_3 exhibits much lower haze than PS/SiO_2 at same particle concentration. The reasons are as follows: first, the difference in refractive indices between PS and Al_2O_3 is smaller than that between PS and SiO_2, therefore less light will be reflected in PS/Al_2O_3

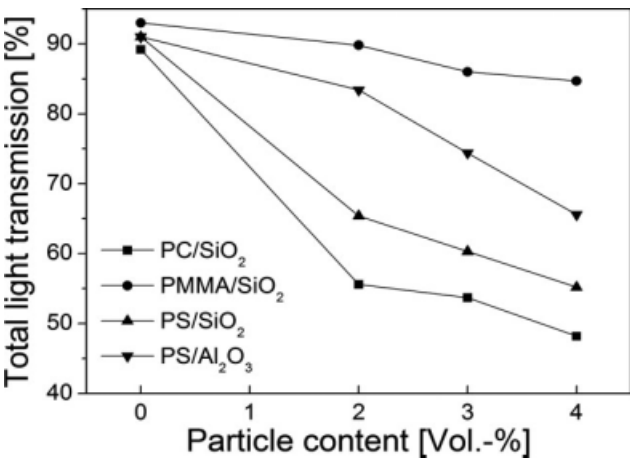

Figure 6 Total light transmittance as a function of particle concentration for all composites.

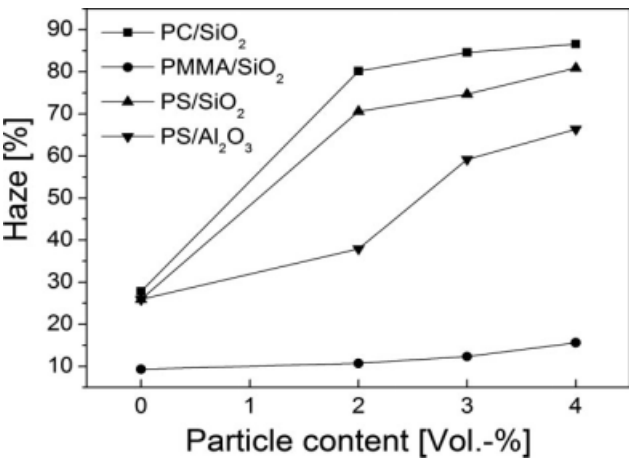

Figure 8 Haze as a function of particle concentration for all composites.

composites than in PS/SiO_2 composites. Second, the main reason for increasing haze is Rayleigh light scattering in composites caused by dispersed particles, which sizes are smaller than the light wavelength used (a condition for Rayleigh scattering).[5,7] According to SEM analysis, the average size of alumina particles (>10 μm) is much larger than the light wavelength used (589 nm), whereas the average size of silica nanoparticles (about 80 nm) is much smaller than the light wavelength used. Therefore, the Rayleigh scattering in PS/Al_2O_3 composites is much weaker than that in PS/SiO_2 composites. In the case of PC/SiO_2 composites, the haze values are obviously increased compared to the other composites because of thermal degradation of PC matrix and large fluctuation of refractive indices.

Figure 9 shows the results of clarity measurements. Interestingly, the clarity of SiO_2-filled composites decreases very slightly as the particle concentration increases. In contrast, the clarity of PS/Al_2O_3 composites decreases drastically, although there is a smaller difference in refractive indices between PS and alumina particles. It is thought that this drastic decrease is caused by increasing size and number of large alumina agglomerates, which reduce the intensity of light beam transmitted through the sample. In silica-filled composites, in which the particle sizes are similar to each other, the result of clarity correlates well with the order of difference in refractive indices.

The relationship between composite transparency and difference in refractive indices is presented in Figure 10. It is evident that both total light transmittance and haze deteriorate with increasing difference in refractive indices independent of particle size (nano vs. micro). Accordingly, one can conclude that the light transmittance and haze are more affected by difference in refractive indices between polymer matrix and particles than by average size of fillers. Different from light transmittance and haze, there is no clear relationship found between clarity and fluctuation of refractive index in all analyzed composites. Comparing the results of PS/SiO_2 composites and PS/Al_2O_3 composites, one can say that the particle sizes play a more important role in composite clarity.

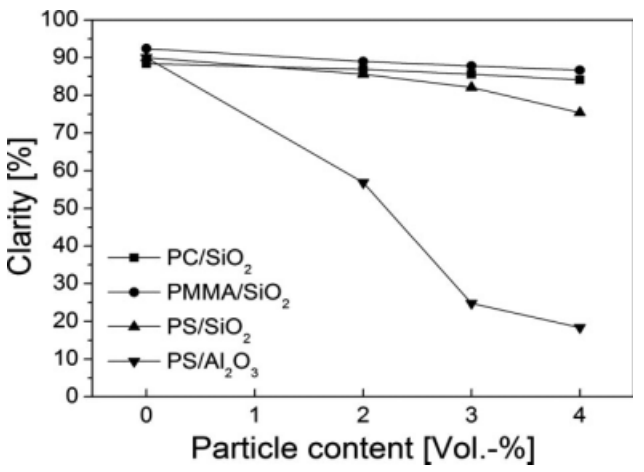

Figure 9 Clarity as a function of particle concentration for all composites.

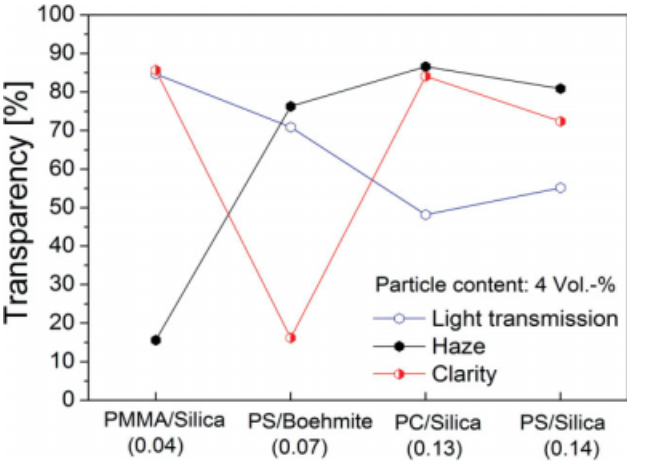

Figure 10 Relationship between transparency and difference in refractive indices based on composites containing 4 vol % particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

In this work, PC/SiO_2, PMMA/SiO_2, PS/SiO_2, and PS/Al_2O_3 composites were produced by melt compounding in Brabender mixer and then optical properties were characterized. According to results achieved, the following conclusions can be drawn:

1. PMMA/SiO_2 nanocomposites exhibit the best optical properties in all investigated composites because of a perfect index-matching. PC/SiO_2 composites show decreased transparency caused by thermal degradation during mixing process and large difference of refractive indices.
2. PS/Al_2O_3 composites show better results of total light transmittance and haze than PS/SiO_2 composites because of better index-matching, but lower clarity because of larger alumina agglomerates.
3. Increasing particle concentration leads to a decrease of composite transparency. The major effect on light transmittance and haze is difference in refractive indices between polymer matrix and particles, whereas the clarity is more affected by particle size than by difference in refractive indices.

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