Nanofiller materials for transparent polymer composites: Influences on the properties and on the transparency— A review

Wolfgang Wildner and Dietmar Drummer

Abstract

Filler materials are widely used in combination with polymer materials. Conventional filler particles generally cause light scattering and absorption because of their optical characteristic or refractive index difference. With nanoparticles (NPs) as a filler material, it is theoretically possible to manufacture transparent compounds due to their small particle dimensions reducing the interaction with light. Nevertheless, the particles tend to build agglomerates and aggregates which reduce the composite's transparency considerably. This review gives an overview of the effect different particle materials have on the properties of transparent polymer composites with consideration of the composite's transparency. There are very few reports on highly transparent and thick (>1 mm) polymer nanocomposites with such an amount of particles that affect other properties of the polymer significantly. In the majority of cases, NPs lead to a significant lower transparency. This indicates that the homogeneous dispersion of the particles is still a major difficulty in producing transparent nanocomposites with enhanced properties.

Keywords

Nanocomposites, transparent polymers, transparent composites, nanofillers, transparent fillers

Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Erlangen, Germany

Corresponding author:

Wolfgang Wildner, Institute of Polymer Technology, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Am Weichselgarten 9, Erlangen 91058, Germany.

Email: wildner@lkt.uni-erlangen.de

Introduction

Nanoparticles (NPs) as a filler for polymers have gained a great deal of attention since 1993 when researchers increased the yield and tensile strength of nylon-6 by an amount of about 2.5 by adding only 7 wt% clay platelets.¹ The main difference in NPs is the enormous specific surface area which is one to two orders of magnitude higher than for conventional fillers.^{2,3} The amount of surface atoms is 20% for a 10 nm particle and increases to a percentage of 80% of all atoms for a particle with a diameter of 2 nm.⁴ A larger surface area leads to a higher surface reactivity.⁵ Therefore, it is possible to improve the polymer's properties with considerably low filler loadings or even to integrate new properties.^{6–8} Moreover, low filler loadings and a filler size far smaller than the wavelength of visible light enable the manufacture of transparent composites.

Nevertheless, scattering and absorption of light by NPs impair the transmittance of a composite. The absorption and scattering cross-section express the efficiency absorption and scattering. In standard spectroscopy measurements, the intensity losses represent the extinction, which is composed of the losses due to absorption and scattering.⁹ The scattering intensity I_S of a particle depends on the following correlation^{10–12}

$$I_S \sim \frac{d^6}{\lambda^4} \quad (1)$$

where d is the particle diameter and λ is the wavelength of light. Therefore, a proper dispersion of the particles in the matrix is very important to reduce their effective diameter. However, homogeneous particle dispersion is one of the main challenges in manufacturing nanocomposites,^{7,13,14} because the particles' high surface energy causes strong interactions between them.¹⁵ There exist different approaches to the dispersion of NPs and the preparation of composites with a polymer matrix. Several methods for the preparation of transparent composites are described by Demir and Wegner¹⁴ and Althues et al.,¹⁶ whereas in situ polymerization and in situ particle processing are mentioned as an advantageous way to avoid particle aggregation. Other routes are the incorporation of NPs into the polymer melt by means of shear mixing with an extruder^{17–19} or the injection of a NP solution into the polymer melt during extrusion.²⁰ Chemically more demanding processes include the improvement of the particle dispersion and stabilization with grafted polymer chains.²¹

The aim of this work is to give an overview of different NP materials for transparent composites and their effect on the composite's properties. Another focus lies on the transparency of these composites, which is critically evaluated with respect to the part thickness.

Following the "Introduction" section, this article summarizes the influence of NPs on transparent polymers sorted by particle material. A table offers an overview of the effects the fillers have on the properties and on the transparency. The different filler materials and the effect on the properties, as well as the contradiction between the composites' enhanced properties and maintained transparency, is discussed in the subsequent section.

Particle materials and their effects on polymer properties

Gold and silver

Silver (Ag) NPs are often used because of their antibacterial properties in different matrix materials.^{22–24} Apart from this, an increase in the degradation temperature of 26 K (thermogravimetric analysis measurements) was observed with a filler content of 2 wt% by Vodnik et al.²⁵ Caseri²⁶ and Zimmermann et al.²⁷ demonstrate that it is possible to decrease the refractive index (RI) of gelatin by the incorporation of gold (Au) particles. At very high contents of 92.9 wt%, the RI is reduced from about 1.54 to 0.96 at 632.8 nm. The absorption and scattering of single metal particles is described in more detail in the study by Van Dijk et al.²⁸ and Nie and Emory.²⁹ This behavior can be applied to the coloring of polymers¹⁴ with Au NPs, whereas the resultative color of the nanocomposite depends on the particle size and geometry.³⁰

Titan oxide

Titan oxide (TiO₂) on the microscale is often used as a white colorant for polymers because it scatters all visible wavelengths.³¹ Nano-TiO₂ in transparent polymers causes absorption primarily in the ultraviolet (UV) region and is therefore often used as an UV absorber for wavelengths below 400 nm.^{19,32–34} Additionally, influences on the RI and the mechanical and thermal properties have been reported. Nussbaumer et al. observed an increase in the RI in poly(vinyl alcohol)^{32,34} and Tao et al. raised the RI of PGMA (poly(glycidyl methacrylate)) and epoxy which also increased the Abbe number of the material.³⁵ Han and Yu³³ reported reduced elongation at break values in poly(ethylene phthalate), whereas Chatterjee¹⁹ showed an increase in the tensile modulus, decomposition temperature, and thermal stability of poly(methyl methacrylate) (PMMA).

Zinc oxide and cerium oxide

These kinds of NPs are utilized to produce luminescent nanocomposites.^{36–41} For cerium ions, the relationships among blueshift, the valence state of ions, and particle size are described by Tsunekawa et al.⁴⁰ Regarding other effects on the composite's properties, an increase of 26°C in the glass transition temperature,³⁹ an increase in the thermal stability,⁴² and an increase in the RI⁴³ were observed with a PMMA matrix. The transmittance of rather thin specimen (0.4 mm thickness, 0.5 wt% zinc oxide (ZnO) quantum dot (QD)) is high.³⁷ On the other hand, thicker specimens have a low transmittance in the visual range (thickness: 3.5 mm, 1 wt% ZnO NP)⁴⁴ or simply a “transparent appearance” (thickness: 3 mm, ZnO QD).³⁸

A remarkable effect of the transmission of composites made of transparent polystyrene (PS) and cerium oxide (CeO₂) NPs was observed by Parlak and Demir.⁴⁵ The transmittance of the thin films showed a first-order exponential decay up to a particle concentration of 20 wt%, as the Rayleigh scattering theory proposes. Higher filling degrees do not impair further the transmission. This fact is explained as a result of

interference in the multiple instances of light scattering by the quasi-ordered internal microstructure, developing at high filling degrees.

Modified tin oxide (ATO and ITO)

The conductivity and antistatic behavior of antimony-doped tin oxide (ATO) NPs dispersed in transparent polymers is described by Wakabayashi et al.⁴⁶ and Sun et al.⁴⁷ These examined films exhibit antistatic properties above a threshold value of only 0.2 vol%.⁴⁶ This is explained by the forming of chain-like aggregates in the NPs. Modified indium tin oxide (ITO) NPs as processed by Zhou et al.⁴⁸ affect the transparency such that both a UV and infrared (IR) absorption occur in poly(urethane acrylate) (PUA) while showing high transmittance values between 500 and 1000 nm (thickness: 0.1 mm).

Iron oxide and cobalt

Iron oxide (Fe_3O_4) NPs^{49–51} and cobalt (Co) NPs⁵² can lead to a ferromagnetic behavior in a composite. Peluso et al.⁵⁰ show that composites starting as iron(II)mercaptides show higher transmittance values in the range from 400 to 900 nm than composites starting as iron(III)mercaptides. High transparency in the composites is observed for wavelengths over 550⁵² or 700 nm.⁵¹ Potential applications mentioned by Barnakov et al.⁵³ can be found in the magneto-optic field or in electromagnetic interference blocking substrates.

Aluminum oxide

Aluminum oxide (Al_2O_3) NPs have a primarily positive effect on the mechanical properties of the composite. They increase the elastic modulus,^{54,55} the yield stress,⁵⁵ and the impact strength.^{56,57} According to Sarwar et al., the optimum loading for the best mechanical properties is 2.5 wt%.⁵⁵

Zirconium oxide

Zirconium oxide (ZrO_2) NPs diversely affect the composite properties. They can lead to improvements to the hardness and scratch resistance (for which a high filling degree of 15 wt% is needed),⁵⁸ enhancements to the mechanical properties,⁵⁹ adjustments to RI,^{59,60} and improvements to thermal properties.^{59,61} The different filler loading of 20 wt% for a variation in the RI between 1.475 to 1.625⁵⁹ and only 1 wt% for a variation between 1.515 and 1.659⁶⁰ proves most remarkable.

Silicon dioxide

Rahman and Padavettan⁶² offer a good summary of property changes in composites with silicon dioxide (SiO_2) particles. The mostly attained property changes are enhanced mechanical properties^{63,64} and influences on the glass transition temperature in both directions.

Cadmium

Composites with NPs containing cadmium (Cd) are mainly prepared to achieve luminescent properties.^{16,65–70} The luminescent properties increase with a good dispersion of the NPs⁶⁸ and primarily depend on the particle concentration^{66,67} and the particle size.^{65,69} The transmittance decreases strongly below a wavelength of 550 nm, whereas the composites have a good transmittance above.^{68,70} Mohan et al.⁷⁰ also investigated the mechanical properties and observed an increase in the tensile modulus.

Zinc sulfide

The main purpose behind using zinc sulfide (ZnS) particles is also luminescent properties^{71,72} or high RI materials.^{73–75} Zhang et al.⁷³ increased the RI of poly(vinylpyrrolidone) linearly from 1.5061 to 1.7523 with an increasing particle content up to 80 wt% while reducing the Abbe number. The transparency of thin films (thickness: 25 μm) above 500 nm was maintained.

Lead sulfide

As with ZnS, lead sulfide (PbS) is used to increase the RI.^{76–78} As such, Zimmermann et al.⁷⁶ and Weibel et al.⁷⁸ claim to have achieved the highest RIs of 2.5 and 2.9 (600 nm), respectively, known for polymeric composite materials. Lü et al.⁷⁷ offered insights into the transparency, indicating their nanocomposite films containing PbS particles exhibit good transparency (>90%) above 600 nm, although the PbS particles exhibit strong absorption below 600 nm in the UV–visible region.

Carbon nanotubes

A great deal of research has been done on transparent polymer composites with CNTs, whose production is described by Sun and Wang.⁷⁹ The authors manufactured electrically conductive transparent films,^{80–84} a transparent composite with enhanced mechanical properties⁸⁵ or a combination of mechanical, electrical, and transparent properties.⁸⁶ Another application reported by Yu et al. lies in advanced materials for packaging with increased mechanical and barrier properties as well as an enhanced decomposition temperature.⁸⁷

Table 1 offers a summary of the affected properties according to particle material with information about the transparency and specimen thickness.

Discussion

Filler materials and properties

As described above, NPs affect the composite properties in a broad range. Additional to the materials of filler and matrix, the achievable properties depend on the filling degree, particle size and shape, processing method, particle dispersion, matrix–particle adhesion and other factors. Nevertheless, Figure 1 gives a comparative overview over the materials

Table 1. Summary of the effects on the composite properties of different filler materials with information about thickness and transparency.

Property	Change	Transmittance	Specimen thickness	Filling degree	Matrix	Filler (size)	References
RI UV absorption	1.52 (polymer) up to 1.61 (34 wt%) New property	Absorbance: 4.1% (11 wt%, 400 nm)	100 μ m	Up to 34 wt%	PVAL	TiO ₂ (2.5 nm)	32
RI Hardness Thermal stability	1.475 up to 1.625 +100% +50°C	97% (550 nm)	100 μ m	20 wt%	PU	ZrO ₂ (3.8 nm)	59
RI	1.54 up to 1.68 (4.6 vol%)	90% (550 nm, 3.8 vol%)	50–70 μ m (transm.) 70–500 nm (RI)	Up to 7.4 vol%	Siloxane-based	ZnS (1–5 nm)	75
RI	1.5–2.49 (632.8 nm)	—	40 nm–2 μ m	Up to 82 wt%	Gelatin	PbS (2–5 nm)	76
RI	1.57–2.06 (632.8 nm)	90% (37 wt%, 600 nm)	1 μ m	0–41.8 wt%	PTU	PbS (<10 nm)	77
RI	Up to 2.9 (632.8 nm)	—	—	88 wt%	PEO	PbS (2–40 nm)	78
RI	1.515–1.659 (acrylate) 1.589–1.679 (epoxy), 633 nm	>90% (86 wt%)	2–5 μ m	Up to 90 wt%	Acrylate-based/ epoxy-based	ZrO ₂ (3–4 nm)	60
RI UV absorption	1.42–1.475 New property	70% (5 mm thickness, 600 nm)	50 μ m–5 mm	20 wt%	Silicone	TiO ₂ (5 nm)	88
RI Thermal properties	1.506–1.752 (80 wt%, 590 nm) Thermal stability of the coupling agent of NPs increases with filler content	85% (70 wt%, 600 nm)	25 μ m	0–80 wt%	PVP	ZnS (3 nm)	73
RI	1.54 (polymer) to 1.92 (95 wt%, 550 nm) Increases	High (antireflectance coating)	52–80 nm	65–95 wt%	Acrylic	CeO ₂ (10–20 nm)	43
RI Scratch resistance	1.542 (polymer) up to 1.568 (47 vol%) Increases with NIP content	80% (600 nm, 15 wt%)	4 mm	0–15 wt%	PDMAA/Si/DVB	ZnS (3 nm)	74

(continued)

Table I. (continued)

Property	Change	Transmittance	Specimen thickness	Filling degree	Matrix	Filler (size)	References
Thermal properties							
Thermal stability	+35°C (Al ₂ O ₃) +40°C (ZnO)	—	—	1 vol%	PMMA	Al ₂ O ₃ (sphere, 20–45 nm) and ZnO (elongated, 20–35 nm)	42
Thermal stability	In N ₂ : +40°C In air: +95°C	95% (600 nm, 20 wt%)	Thin	0–20 wt%	PMMA	ZrO ₂ /SiO ₂ (<100 nm)	61
Thermal stability UV absorption	+25°C (1 wt%) New property	2% (1 wt%) 50% (0.01 wt%) <90% (0.01 wt%, prepolymer procedure, 600 nm)	3.5 mm	Up to 1 wt%	PMMA	ZnO (75 nm)	44
Glass temperature Photoluminescence	+26°C New property	—	—	3.3 wt%	PMMA	ZnO (6–7 nm)	39
Tensile modulus decomposition temperature	+95% +11%	—	0.3 mm	0–15 wt%	PMMA	TiO ₂ (5 nm)	19
Glass temperature UV absorption	+23% New property	—	—	—	—	—	—
Young modulus Tensile strength UV absorption	+30% +100% New property	80% (2 wt%, 600 nm)	0.15 mm	2 wt%	PC	AlO ₂ (whisker: diameter = 3 nm, length = 2800 nm)	54
Young modulus Glass temperature Tensile strength	+41% (5 wt%) +37% (15 wt%) +41% (2.5 wt%)	87% (600 nm, 15 wt%)	0.12–0.29 mm	0–15 wt%	PA	Al ₂ O ₃	55

(continued)

Table 1. (continued)

Property	Change	Transmittance	Specimen thickness	Filling degree	Matrix	Filler (size)	References
Strength	+21%	71% (600 nm)	50 μ m	0.5 wt%	PAEK	MWNT (diameter: 10–20 nm, length: 5–20 μ m)	85
Elongation at break	+100%						
Impact strength	+126% (1 wt%)	52% (1 wt%, 600 nm)	2 mm	1 or 2 wt%	PC	Al ₂ O ₃ (96 nm)	56
Impact resistance	Increases with the number of layers and addition of NP in the layer bonding adhesive	88% (2 layers) 65% (10 layers, 600 nm)	2 mm pure PMMA layers, bonded with NP adhesive	2 wt% in adhesive	PMMA, styrene, SAN	Alumina (35 nm)	57
Hardness	+40%	—	—	3 wt%	PMMA	SiO ₂ (63 nm)	63
Elastic modulus	+25%						
Tensile strength	+10% (3 wt%)	82% (600 nm, 3 wt%)	Films	1–5 wt%	COC	SiO ₂ (8 nm)	64
Glass temperature	+6% (3 wt%)						
Scratch resistance	Higher						
Coefficient of friction	Lower						
Hardness	Increases	80% (600 nm, 15 wt%)	—	0–15 wt%	PMMA	ZrO ₂ (4 nm)	58
Scratch resistance	Increases						
Tensile modulus	+52%	High	—	—	Epoxy	CdSe-CdS-ZnS core–multi-shell (3–10 nm)	70
Luminescence	New property						
Elastic modulus	+52%	—	100 nm	0–15 wt%	PS	SiO ₂ (14 nm)	89
Yield stress	+14%						
Fracture strain	+257%						

(continued)

Mechanical properties

Table 1. (continued)

Property	Change	Transmittance	Specimen thickness	Filling degree	Matrix	Filler (size)	References
Luminescence UV absorption	New property New property	90% (600 nm)	4 mm	0.5 wt%	PMMA	ZnO (2.3 nm)	37
Luminescence	New property	30% (0.1 ppm, 600 nm)	5 mm	0.02–0.1 ppm	PSO	CdS (6 nm)	66
Luminescence	New property	65% (1.2 wt%, 600 nm)	4 mm	0–1.2 wt%	Epoxy	CdSe (4 nm)	68
Photoluminescence Emitting layer of LED	New property New property	High	50 nm (LED)	Zn: 8.2 wt% Cu: 0.12 wt%	Sulphonated PS	ZnS: Cu (3 nm)	71
Conductivity	10^{-2} S/cm (50 vol%)	75% (50 vol%, 1.3 μ m thick), 17% (50 vol%, 3.4 μ m thick), 600 nm	1–16 μ m (coating)	0–50 vol%	Poly(vinyl acetate- acrylic) (PVAc- co-acrylic)	ATO (15 nm)	47
Permittivity	+46%	>85% above 400 nm	0.127 mm	0.26 wt%	PMMA	SWNT	80
Antistatic properties	Threshold value: 0.2 vol%	91% (0.8 vol%, total luminous transmittance)	2 μ m	0–0.8 vol%	Acrylate	ATO (8 nm)	46
Electrical conductivity Power conversion efficiency of an organic solar cell	Sheet resist: –60% +30%	94% (600 nm)	Thin films	—	PEDOT:PPS	SWNT	81
Conversion efficiency of an organic solar cell	+20%	High (>600 nm)	20 nm	—	PEDOT:PSS	Ag (13 nm)	90

(continued)

Table 1. (continued)

Property	Change	Transmittance	Specimen thickness	Filling degree	Matrix	Filler (size)	References
Magnetic properties	New property	"Good, but brown colored" (>550 nm)	1 mm	3–15 wt%	PS	Fe ₃ O ₄ (acicular, 10 × 50 nm and spherical, 6 nm)	50
Magnetic properties	New property	"Quite" transparent (>550 nm)	100 µm	5–15 wt%	PS	Fe ₃ O ₄ (10 × 50 nm)	51
Magneto-optical properties: Faraday rotation spectra	Red shift with larger particles	Increasing absorption >600 nm	100–300 µm	—	PMMA	Fe ₃ O ₄ (8–200 nm)	53
Transparency at high loadings	—	Decreases to 75% (20 wt%), then stays constant (up to 95 wt%); 550 nm	2.5 µm	Up to 95 wt%	PS	CeO ₂ (20 nm)	45
UV and IR absorption	New property	85% (9 wt%, 600 nm)	100 µm	0–9 wt%	PUA	ITO (163 nm)	48
UV absorption	New property	—	Fibers and fabric	0–2 wt%	PET	TiO ₂	33
Tensile strength	—11%	—	—	—	—	—	—
Optical properties	—	—	—	—	—	—	—
Oxygen barrier	New property	93% (77 wt%, 135 nm thickness, 565 nm)	1.2–230 nm (several layers)	77–84 wt%	PEI	MMT	91

PET: poly(ethylene phthalate); PUA: poly(urethane acrylate); PMMA: poly(methyl methacrylate); ZNO: zinc oxide; CeO₂: cerium oxide; ATO: antimony-doped tin oxide; ITO: indium tin oxide; IR: infrared; UV: ultraviolet; Fe₃O₄: iron oxide; CO: cobalt; Al₂O₃: aluminum oxide; ZrO₂: zirconium oxide; SiO₂: silicon dioxide; ZnS: zinc sulfide; PbS: lead sulfide; PU: polyurethane; PTU: polythiourethane; PEO: poly(ethylene oxide); PDMAA/St/DVB: poly(*N,N*-dimethylacrylamide)/styrene/divinylbenzene; PC: polycarbonate; PA: polyamide; PAEK: poly(aryl ether ketone); SAN: styrene acrylonitrile; PSC: polysiloxane; PEDOT: PPS; poly(3,4-ethylenedioxythiophene); poly(styrenesulfonate); PEI: polyethylenimine; PVA: poly(vinyl alcohol); PVP: poly(vinylpyrrolidone); MMT: sodium montmorillonite; MWNT: multiwalled carbon nanotube; SWNT: single-walled carbon nanotube; Ag: silver; LED: light-emitting diode; Al₂O₃: aluminum oxide; CdSe: cadmium selenide; CdS: cadmium sulfide.

Figure 1. Percentage changes of properties in dependence of the filler material including the references.

listed in Table 1 and their effects on the nanocomposites properties. The figure shows that specific materials diversely affect the properties due to the numerous additional influences mentioned above. However, some materials are particularly suitable to improve specific properties, like Al₂O₃ and SiO₂ for better mechanical properties or PbS for a higher RI.

Influence of the particles on the transparency

According to Rayleigh scattering, the scattering section C_s of a particle merely depends on its diameter d , the RI relation m between particle and matrix and the wavelength λ ¹²

$$C_s = \frac{2\pi^5 d^6}{3\lambda^4} \left(\frac{m^2 - 1}{m^2 + 1} \right)^2 \quad (2)$$

Consequently, the only possibilities to reduce scattering in the visual range are to reduce the particle size (improving the particle dispersion has the same effect) or matching the RI between particles and matrix. Promising results with RI matching were achieved by synthesizing core-shell particles^{92–94} or polymer-graft modifications of fillers, both with the matrix' RI is in between the RIs of core and shell or of particles and grafted polymer chains.⁹⁵ Effective medium theory describes the RI of core-shell particles⁹⁵ and polymer-graft modified particles.⁹⁴ The theory enables the calculation of an effective RI out of the different materials' properties of the particle to match it's RI to the matrix' RI. Nevertheless, limitations have to be considered if the particles size is comparable to the wavelength of the incident light, due to additional Mie scatterings by the core.⁹⁶

Furthermore, some materials absorb shares of the incident light. Only dielectric particles with zero electrical conductivity are completely nonabsorbing.¹² The absorption of a material is expressed by the material's complex RI. Nevertheless, almost dielectric materials like glass have a negligible dielectric loss in the visual range and therefore hardly absorb the light. On the contrary, metal particles, even with small diameters, have a strong wavelength-dependent absorption in the visual range due to the oscillation of free surface electrons.^{97–99} The absorption cross-section of particles varies as d^3 . Therefore, the absorption of very small particles exceeds their total scattering.^{28,100,101}

Transparency and enhanced properties

Regarding the specimen from the listed references in this article, most authors analyze very thin specimen or give no exact information about the thickness. However, the thickness is crucial for classifying the transparency gains, as transmission decreases strongly with it. Investigations of thin films have several advantages: The specimens enable easy preparation from a polymer solution via drying or melt spinning and thin films require only a small amount of NPs. In addition, a high rate of transparency can be easily achieved.

In few of the analyzed papers, specimens with a thickness of ≥ 1 mm are described and information about the transparency is given.^{37,44,50,56,66,68,74,88,94} These specimens mostly have very low NP content if they exhibit a relatively high amount of transparency. With this low particle loading, hardly any influence on properties other than the specimen's optical characteristics (luminescence and UV absorption) is ascertainable. For example, Anžlovar et al.⁴⁴ reach high transparency values with a filler content of 0.01 wt%, but for a significant change in thermal stability, a filler content of 1 wt% is needed. However, with this filler content, the transparency at 500 nm is almost zero. Magnetic behavior is reported by Peluso et al.⁵⁰ who claim that the 1-mm thick specimens have perfect transparency above a wavelength of 550 nm, but there is no specific transparency value given and the specimens are simply "brown colored". Chandra et al.⁵⁶ attained an increased impact strength but also have a high transmission loss

(transmittance: 40% at 500 nm and 1 wt% of Al_2O_3 NPs). There is little information about transparent thick specimens with NP filling that enhances the properties: Guan et al.⁷⁴ describe 4-mm thick, highly transparent composites with a filling degree of up to 15 wt% ZnS NPs which had been prepared through one-pot in situ bulk polymerization. The particles cause an increase in RI and in glass transition temperature of the transparent composite. Also thick (5 mm), highly filled (20 wt%) specimens with enhanced RI are described by Li et al.⁸⁸ They achieved a good dispersion in silicone by using bimodal-poly(dimethyl siloxane)-brush-grafted TiO_2 particles.

On the other hand, optical properties can be affected by very low filling degrees, which maintain the transparency in the visual range. Luminescent properties were integrated by Zou et al. with very low filling degrees of 0.3 wt% and by maintaining the transparency (73% for 530 nm).⁶⁸ As shown by Anžlovar et al.⁴⁴ UV absorption is possible with a very low ZnO content of 0.01 wt% while exhibiting high transparency values in the visual range.

As mentioned above, more recent approaches focus on core-shell particles and polymer-graft modification of particles. Li et al.⁹⁴ achieved high rates of transparency (70% at 500 nm) with a filling degree of 1 wt% of $\text{SiO}_2/\text{TiO}_2$ core-shell particles and a specimen thickness of 4 mm. It was possible to control the RI of the total particle with the ratio of core to shell. If the RI does not match the matrix, the specimen has a completely opaque appearance. Incel et al.⁹² manufactured highly transparent PS films, filled with ceria/silica hybrid particles. The particles have the same RI as the matrix due to their controlled core-shell ratio. The approach of RI matching by grafting polymer chains which are different to the polymer matrix is described by Parlak and Demir.¹⁰² and Dang et al.⁹⁵ Methods of synthesis, analysis, and some properties of nanocomposites with polymer-grafted NPs are summarized by Kumar et al.²¹ An increase in the mechanical properties observed by Maillard et al.⁸⁹ was attributed to the uniform dispersion and strong interfacial binding due to the polymer-grafted NPs. The achieved transparency values are promising. However, in combination with transparent polymers, most authors focus on the transparency only and the impact on other properties is scarcely investigated. Furthermore, these particles are more challenging to synthesize, so they are produced in very small quantities only. To investigate the role of film thickness and to validate these results on a macroscopic scale, it would be necessary to produce larger quantities of these particles.²¹

Conclusion

NPs are widely used in research to enhance material properties and to functionalize transparent polymers. For a significant impact on the mechanical and thermal properties, for example, the glass transition temperature or decomposition temperature, very low filler loadings compared to conventional fillers are necessary. However, there are considerable shortcomings in the transparency after integrating NPs into the transparent polymers. Despite several approaches to dispersing the particles homogeneously, achieving transparency for thicker parts while simultaneously enhancing other properties significantly has largely remained an insurmountable hurdle. Also, thin films mostly

show a significant decrease in the transmission. Only optical properties such as luminescence and UV absorption can be included with very low filler contents enabling to maintain the polymer's transparency. These shortcomings in the transmission of transparent nanocomposites indicate that the homogeneous dispersion of the particles remains a major difficulty, which has not yet been satisfactorily solved on a macroscopic level. However, there are promising approaches in NP chemistry to improve their dispersion and/or to adapt their RI to the matrix in order to achieve high transparency values. However, until now, there is sparse information available about the effect on other properties. Consequently, future research should focus on the upscaling of the particle production and on a comprehensive analysis of the macroscopic nanocomposites properties to identify and exploit their potential in practical applications.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG) through the Cluster of Excellence Engineering of Advanced Materials.

ORCID iD

Wolfgang Wildner <https://orcid.org/0000-0002-5251-8720>

References

1. Kojima Y, Usuki A, Kawasumi M, et al. Mechanical properties of nylon 6-clay hybrid. *J Mater Res* 1993; 8: 1185–1189.
2. Rothon R. *Particulate-filled polymer composites*. Akron: Rapra Technology, 2003.
3. Siegel RW and Hu E. *Nanostructure science and technology: R & D status and trends in nanoparticles, nanostructured materials and nanodevices*. Dordrecht: Springer Netherlands, 2013.
4. Ichinose N, Ozaki Y and Kashu S. *Superfine particle technology*. London: Springer Verlag, 1992.
5. Gilbertson LM, Albalghiti EM, Fishman ZS, et al. Shape-Dependent surface reactivity and antimicrobial activity of nano-cupric oxide. *Environ Sci Technol* 2016; 50: 3975–3984.
6. Bonanni V, Bonetti S, Pakizeh T, et al. Designer magnetoplasmonics with nickel nanoferro-magnets. *Nano Lett* 2011; 11: 5333–5338.
7. Ajayan PM, Schadler LS and Braun PV. *Nanocomposite science and technology*. Weinheim: Wiley VCH, 2003.
8. Friedrich K, Fakirov S and Zhang Z. *Polymer composites: From nano- to macro-scale*. New York: Springer US, 2005.
9. Evanoff DD Jr, and Chumanov G. Size-controlled synthesis of nanoparticles. 2. Measurement of extinction, scattering, and absorption cross sections. *J Phys Chem B* 2004; 108: 13957–13962.
10. Meeten GH. *Optical properties of polymers*. New York: Elsevier Applied Science Publishers, 1986.
11. Schärfl W. *Light scattering from polymer solutions and nanoparticle dispersions*. Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg, 2007.
12. Hulst H. *Light scattering by small particles*. New York: Dover-Publications, 1981.

13. Uddin MF and Sun CT. Effect of nanoparticle dispersion on mechanical behavior of polymer nanocomposites. In: *50th AIAA/ASME/ASCE/AHS/ASC Structures, structural dynamics and materials conference*. Palm Springs, California, 4-7 May 2009. USA.
14. Demir MM and Wegner G. Challenges in the preparation of optical polymer composites with nanosized pigment particles: a review on recent efforts. *Macromolecular Materials and Engineering* 2012; 297: 838–863.
15. Liu J, Gao Y, Cao D, et al. Nanoparticle dispersion and aggregation in polymer nanocomposites: insights from molecular dynamics simulation. *Langmuir* 2011; 27: 7926–7933.
16. Althues H, Henle J and Kaskel S. Functional inorganic nanofillers for transparent polymers. *Chem Soc Rev* 2007; 36: 1454–1465.
17. Shah RK and Paul DR. Nylon 6 nanocomposites prepared by a melt mixing masterbatch process. *Polymer* 2004; 45: 2991–3000.
18. Zhao H and Li RKY. A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites. *Polymer* 2006; 47: 3207–3217.
19. Chatterjee A. Properties improvement of PMMA using nano TiO₂. *J Appl Polym Sci* 2010; 118: 2890–2897.
20. Bacher A, Berkei M, Drude H, et al. *Direktprozess zur herstellung von nanosuspensionen und deren zudosierung in thermoplastische matrices zur herstellung von nanocomposites*. Pfinztal: Fraunhofer Verlag, 2011.
21. Kumar SK, Jouault N, Benicewicz B, et al. Nanocomposites with polymer grafted nanoparticles. *Macromolecules* 2013; 46: 3199–3214.
22. Pinto RJB, Fernandes SCM, Freire CSR, et al. Antibacterial activity of optically transparent nanocomposite films based on chitosan or its derivatives and silver nanoparticles. *Carbohydr Res* 2012; 348: 77–83.
23. Akhavan O. Lasting antibacterial activities of Ag-TiO₂/Ag/a-TiO₂ nanocomposite thin film photocatalysts under solar light irradiation. *J Colloid Interf Sci* 2009; 336: 117–124.
24. Chan CMN, Cheng HS, Djurišić AB, et al. Multicomponent antimicrobial transparent polymer coatings. *J Appl Polym Sci* 2011; 122: 1572–1578.
25. Vodnik VV, Vuković JV and Nedeljković JM. Synthesis and characterization of silver-poly(-methylmethacrylate) nanocomposites. *Colloid Polym Sci* 2009; 287: 847–851.
26. Caseri W. Nanocomposites of polymers and metals or semiconductors: historical background and optical properties. *Macromol Rapid Comm* 2000; 21: 705–722.
27. Zimmermann L, Weibel M, Caseri W, et al. Polymer nanocomposites with “ultralow” refractive index. *Polym Advan Technol* 1993; 4: 1–7.
28. Van Dijk MA, Tchegbotareva AL, Orrit M, et al. Absorption and scattering microscopy of single metal nanoparticles. *Phys Chem Chem Phys* 2006; 8: 3486–3495.
29. Nie S and Emory SR. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science* 1997; 275: 1102–1106.
30. Liu Y, Mills EN and Composto RJ. Tuning optical properties of gold nanorods in polymer films through thermal reshaping. *J Mater Chem* 2009; 19: 2704–2709.
31. Murphy J. *Additives for plastics handbook*. New York: Elsevier Science, 2001.
32. Nussbaumer RJ, Caseri WR, Smith P, et al. Polymer-TiO₂ nanocomposites: a route towards visually transparent broadband UV filters and high refractive index materials. *Macromol Mater Eng* 2003; 288: 44–49.
33. Han K and Yu M. Study of the preparation and properties of UV-blocking fabrics of a PET/TiO₂ nanocomposite prepared by in situ polycondensation. *J Appl Polym Sci* 2006; 100: 1588–1593.

34. Nussbaumer RJ. *Synthese und charakterisierung von rutilnanopartikeln und deren einbau in transparente polymer-nanoverbundwerkstoffe*. Zürich: Eidgenössische Technische Hochschule, 2004.
35. Tao P, Li Y, Rungta A, et al. TiO₂ nanocomposites with high refractive index and transparency. *J Mater Chem* 2011; 21: 18623–18629.
36. Althues H. Lumineszierende, transparente Nanokomposite—Synthese und Charakterisierung. *Fakultät Mathematik und Naturwissenschaften*. Dresden: Technischen Universität Dresden, 2007.
37. Zhang Y, Wang X, Liu Y, et al. Highly transparent bulk PMMA/ZnO nanocomposites with bright visible luminescence and efficient UV-shielding capability. *J Mater Chem* 2012; 22: 11971–11977.
38. Matsuyama K, Mishima K, Kato T, et al. Transparent polymeric hybrid film of ZnO nanoparticle quantum dots and PMMA with high luminescence and tunable emission color. *J Colloid Interf Sci* 2012; 367: 171–177.
39. Sato M, Kawata A, Morito S, et al. Preparation and properties of polymer/zinc oxide nanocomposites using functionalized zinc oxide quantum dots. *Eur Polym J* 2008; 44: 3430–3438.
40. Tsunekawa S, Wang JT, Kawazoe Y, et al. Blueshifts in the ultraviolet absorption spectra of cerium oxide nanocrystallites. *Jpn J Appl Phys* 2003; 94: 3654–3656.
41. Sarapulova O, Sherstiuk V, Shvalagin V, et al. Photonics and nanophotonics and information and communication technologies in modern food packaging. *Nanoscale Res Lett* 2015; 10: 229.
42. Viratyaporn W and Lehman RL. Effect of nanoparticles on the thermal stability of PMMA nanocomposites prepared by in situ bulk polymerization. *J Therm Anal Calorim* 2011; 103: 267–273.
43. Krogman KC, Druffel T and Sunkara MK. Anti-reflective optical coatings incorporating nanoparticles. *Nanotechnology* 2005; 16: S338–S343.
44. Anžlovar A, Orel ZC and Žigon M. Sub micrometer and nano ZnO as filler in PMMA materials. *Mater Tehnol* 2011; 45: 269–274.
45. Parlak O and Demir MM. Anomalous transmittance of polystyrene-ceria nanocomposites at high particle loadings. *J Mater Chem C* 2013; 1: 290–298.
46. Wakabayashi A, Sasakawa Y, Dobashi T, et al. Optically transparent conductive network formation induced by solvent evaporation from tin-oxide-nanoparticle suspensions. *Langmuir* 2007; 23: 7990–7994.
47. Sun J, Gerberich WW and Francis LF. Electrical and optical properties of ceramic-polymer nanocomposite coatings. *J Polym Sci, Part B-Polym Phys* 2003; 41: 1744–1761.
48. Zhou H, Wang H, Tian X, et al. Preparation of UV-curable transparent poly(urethane acrylate) nanocomposites with excellent UV/IR shielding properties. *Compos Sci Technol* 2014; 94: 105–110.
49. Gass J, Poddar P, Almand J, et al. Superparamagnetic polymer nanocomposites with uniform Fe₃O₄ nanoparticle dispersions. *Adv Funct Mater* 2006; 16: 71–75.
50. Peluso A, Pagliarulo V, Carotenuto G, et al. Synthesis and characterization of polymer embedded iron oxide nanocomposites. *Microw Opt Techn Let* 2009; 51: 2774–2777.
51. Carotenuto G, Pepe G, Davino D, et al. Transparent-ferromagnetic thermoplastic polymers for optical components. *Microw Opt Techn Let* 2006; 48: 2505–2508.
52. Horikawa A, Yamaguchi K, Inoue M, et al. Magneto-optical effect of films with nano-clustered cobalt particles dispersed in PMMA plastics. *Mat Sci Eng A* 1996; 217–218: 348–352.

53. Barnakov YA, Scott BL, Golub V, et al. Spectral dependence of Faraday rotation in magnetite-polymer nanocomposites. *J Phys Chem Solids* 2004; 65: 1005–1010.
54. Hakimelahi HR, Hu L, Rupp BB, et al. Synthesis and characterization of transparent alumina reinforced polycarbonate nanocomposite. *Polymer* 2010; 51: 2494–2502.
55. Sarwar MI, Zulfiqar S and Ahmad Z. Investigating the property profile of polyamide-alumina nanocomposite materials. *Scripta Mater* 2009; 60: 988–991.
56. Chandra A, Turng LS, Li K, et al. Fracture behavior and optical properties of melt compounded semi-transparent polycarbonate (PC)/alumina nanocomposites. *Compos Part A-Appl S* 2011; 42: 1903–1909.
57. Rai KN and Singh D. Impact resistance behavior of polymer nanocomposite transparent panels. *J Compos Mater* 2009; 43: 139–151.
58. Hu Y, Zhou S and Wu L. Surface mechanical properties of transparent poly(methyl methacrylate)/zirconia nanocomposites prepared by in situ bulk polymerization. *Polymer* 2009; 50: 3609–3616.
59. Xu K and Hu YQ. Fabrication of transparent Pu/ZrO₂ nanocomposite coatings with high refractive index. *Chinese J Polym Sci (English Edition)* 2010; 28: 13–20.
60. Kudo S, Nagase K, Kubo S, et al. Optically transparent and refractive index-tunable ZrO₂/photopolymer composites designed for ultraviolet nanoimprinting. *Jpn J Appl Phys* 2011; 50, 06GK12-1 to 06GK12-7.
61. Wang H, Xu P, Zhong W, et al. Transparent poly(methyl methacrylate)/silica/zirconia nanocomposites with excellent thermal stabilities. *Polym Degrad Stabil* 2005; 87: 319–327.
62. Rahman IA and Padavettan V. Synthesis of Silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites—a review. *J Nanomater* 2012; 1–15.
63. Stojanovic D, Orlovic A, Markovic S, et al. Nanosilica/PMMA composites obtained by the modification of silica nanoparticles in a supercritical carbon dioxide-ethanol mixture. *J Mater Sci* 2009; 44: 6223–6232.
64. Roy S, Das T, Yue CY, et al. Transparent cyclic olefin copolymer/silica nanocomposites. *Polym Int* 2014; 63: 327–332.
65. Zhang H, Cui Z, Wang Y, et al. From water-soluble CdTe nanocrystals to fluorescent nanocrystal-polymer transparent composites using polymerizable surfactants. *Adv Mater* 2003; 15: 777–780.
66. Shen ZR, Li YL, Liu JB, et al. Transparent luminescent bulk nanocomposites of polysiloxane embedded with CdS nanocrystallines by a direct dispersion process. *Nanoscale* 2012; 4: 1652–1657.
67. Zhang Y, Jiang D, Wang H, et al. In situ synthesis of transparent fluorescent cadmium sulfide-poly(arylene ether ketone) nanocomposite hybrids. *Adv Polym Sci* 2013; 25: 879–885.
68. Zou W, Du ZJ, Li HQ, et al. A transparent and luminescent epoxy nanocomposite containing CdSe QDs with amido group-functionalized ligands. *J Mater Chem* 2011; 21: 13276–13282.
69. Lee J, Sundar VC, Heine JR, et al. Full color emission from II-VI semiconductor quantum dot-polymer composites. *Adv Mater* 2000; 12: 1102–1105.
70. Mohan S, Oluwafemi OS, Songca SP, et al. Facile synthesis of transparent and fluorescent epoxy-CdSe-CdS-ZnS core-multi shell polymer nanocomposites. *New J Chem* 2014; 38: 155–162.
71. Huang J, Yang Y, Xue S, et al. Photoluminescence and electroluminescence of ZnS: Cu nanocrystals in polymeric networks. *Appl Phys Lett* 1997; 70: 2335–2337.

72. Dai Prè M, Martucci A and Leoni M. Synthesis and characterization of ZnS: Mn nanoparticles. *Proceedings of SPIE—The International Society for Optical Engineering, Photonics for Solar Energy Systems III*, Brussels, Belgium, 13–15 April 2010.
73. Zhang Q, Goh ESM, Beuerman R, et al. Development of optically transparent ZnS/poly(vinylpyrrolidone) nanocomposite films with high refractive indices and high Abbe numbers. *J Appl Polym Sci* 2013; 129: 1793–1798.
74. Guan C, Lü C, Cheng Y, et al. A facile one-pot route to transparent polymer nanocomposites with high ZnS nanophase contents via in situ bulk polymerization. *J Mater Chem* 2009; 19: 617–621.
75. Sergienko N, Godovsky D, Zavin B, et al. Nanocomposites of ZnS and poly-(dimethyl)-block-(phenyl)siloxane as a new high-refractive index polymer media. *Nanoscale Res Lett* 2012; 7: 1–7.
76. Zimmermann L, Weibel M, Caseri W, et al. High refractive index films of polymer nanocomposites. *J Mater Res* 1993; 8: 1742–1748.
77. Lü C, Guan C, Liu Y, et al. PbS/polymer nanocomposite optical materials with high refractive index. *Chem Mater* 2005; 17: 2448–2454.
78. Weibel M, Caseri W, Suter UW, et al. Preparation of polymer nanocomposites with “Ultrahigh” refractive index. *Polymers for Advanced Technologies* 1991; 2: 75–80.
79. Sun J and Wang R. *Syntheses and applications of carbon nanotubes and their composites*. Rijeka: INTECH, 2013.
80. Clayton LM, Sikder AK, Kumar A, et al. Transparent poly(methyl methacrylate)/single-walled carbon nanotube (PMMA/SWNT) composite films with increased dielectric constants. *Adv Funct Mater* 2005; 15: 101–106.
81. Jin SH, Cha SI, Jun GH, et al. Non-covalently functionalized single walled carbon nanotube/poly(3, 4ethylenedioxythiophene): poly(styrenesulfonate) nanocomposites for organic photovoltaic cell. *Synthetic Met* 2013; 181: 92–97.
82. Huang S, Li L, Yang Z, et al. A new and general fabrication of an aligned carbon nanotube/polymer film for electrode applications. *Adv Mater* 2011; 23: 4707–4710.
83. Zhang Y, Li Z, Li H, et al. Effect of carbon nanotubes shape on the properties of multiwall carbon nanotubes/polyethylene flexible transparent conductive films. *J Mater Sci-Mater El* 2014; 25: 2692–2696.
84. Kim DH and Park SY. In-situ preparation of multi-walled carbon nanotube (MWNT)/cellulose nanocomposites and their physical properties. *Fiber Polym* 2013; 14: 566–570.
85. Du Y, Hu N, Zhou H, et al. Dispersion of multi-walled carbon nanotubes in poly(aryl ether ketone) obtained by in situ polymerization. *Polym Int* 2009; 58: 832–837.
86. Park C, Ounaies Z, Watson KA, et al. Dispersion of single wall carbon nanotubes by in situ polymerization under sonication. *Chem Phys Lett* 2002; 364: 303–308.
87. Yu HY, Qin ZY, Sun B, et al. Reinforcement of transparent poly(3-hydroxybutyrate-co-3-hydroxyvalerate) by incorporation of functionalized carbon nanotubes as a novel bionanocomposite for food packaging. *Compos Sci Technol* 2014; 94: 96–104.
88. Li Y, Tao P, Viswanath A, et al. Bimodal surface ligand engineering: the key to tunable nanocomposites. *Langmuir* 2013; 29: 1211–1220.
89. Maillard D, Kumar SK, Fragneaud B, et al. Mechanical properties of thin glassy polymer films filled with spherical polymer-grafted nanoparticles. *Nano Lett* 2012; 12: 3909–3914.
90. Kim SS, Na SI, Jo J, et al. Plasmon enhanced performance of organic solar cells using electrodeposited Ag nanoparticles. *Appl Phys Lett* 2008; 93: 073307-1 to 073307-3.
91. Priolo MA, Gamboa D and Grunlan JC. Transparent clay-polymer nano brick wall assemblies with tailorable oxygen barrier. *ACS Appl Mater Inter* 2010; 2: 312–320.

92. Incel A, Güner T, Parlak O, et al. Null extinction of Ceria@ silica hybrid particles: transparent polystyrene composites. *ACS Appl Mater Inter* 2015; 7: 27539–27546.
93. Small A, Hong S and Pine D. Scattering properties of core-shell particles in plastic matrices. *J Polym Sci Part B-Pol Phys* 2005; 43: 3534–3548.
94. Li YQ, Fu SY, Yang Y, et al. Facile synthesis of highly transparent polymer nanocomposites by introduction of core-shell structured nanoparticles. *Chem Mater* 2008; 20: 2637–2643.
95. Dang A, Ojha S, Hui CM, et al. High-transparency polymer nanocomposites enabled by polymer-graft modification of particle fillers. *Langmuir* 2014; 30: 14434–14442.
96. Zhang H, Zhu P, Xu Y, et al. Effective medium theory for random media composed of two-layered spheres. *J Opt Soc Am A* 2011; 28: 2292–2297.
97. Jain PK, Lee KS, El-Sayed IH, et al. Calculated absorption and scattering properties of gold nanoparticles of different size, shape, and composition: Applications in biological imaging and biomedicine. *J Phys Chem B* 2006; 110: 7238–7248.
98. El-Sayed MA. Some interesting properties of metals confined in time and nanometer space of different shapes. *Acc Chem Res* 2001; 34: 257–264.
99. Bohren CF and Huffman DR. *Absorption and scattering of light by small particles*. Hoboken: Wiley, 1998.
100. Fan X, Zheng W and Singh DJ. Light scattering and surface plasmons on small spherical particles. *Light Sci Appl*. 2014; 3: e179.
101. van de Hulst HC. *Light scattering by small particles*. New York: Dover Publications, 1981.
102. Parlak O and Demir MM. Toward transparent nanocomposites based on polystyrene matrix and PMMA-grafted CeO₂ nanoparticles. *ACS Appl Mater Inter* 2011; 3: 4306–4314.