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Polymer Particles with a Low Glass Transition Temperature Containing Thermoset Resin Enable Powder Coatings at Room Temperature

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Abstract

Epoxy-based powder coatings are an attractive alternative to solvent-borne coatings. Here, in-house synthesized low glass transition temperature (T_g) particles containing epoxy resin and polymethyl methacrylate formed coatings at room temperature upon impact with a surface. Suspension polymerization was used to prepare particles as a function of diglycidyl ether of bisphenol A (DGEBA) and methyl methacrylate ratios. Higher incorporation of DGEBA decreased the T_g to below $\sim 20^\circ\text{C}$ and eliminated the need to heat the particles and/or aluminum substrates to form coatings. Using an electrostatic powder coating apparatus, a $\sim 70\%$ particle deposition efficiency was achieved on aluminum substrates heated to 200°C . Whereas, at room temperature, high-speed single particle impact experiments proved that particle bonding occurred at a critical velocity of 438 m/s , comparable to commercial cold spray technologies. The in-house synthesized particles used in this study hold potential in traditional and emerging additive manufacturing applications.

GRAPHICAL ABSTRACT

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Keywords

Additive manufacturing; Glass transition temperature; Epoxy; Particle; Thermoset

INTRODUCTION

Polymer coatings, especially solvent-borne coatings, protect industrial and architectural surfaces in marine environments,¹ automotive applications,² and residential settings.³ However, if the solvent contains even a trace amount of volatile organic compounds (VOCs), there can be serious concerns about health hazards and environmental pollution.⁴ Therefore, the global market of powder coatings, which do not emit VOCs, is expected to grow from 2.25 to 3.82 million metric tons by 2023.⁵ While a number of common chemistries are used for thermosetting powder coatings (i.e., epoxy, polyester, acrylic, polyurethane),⁶ due to their high durability and superior chemical, adhesion, and thermal properties,⁷ epoxy-based coatings are extensively applied to industrial equipment, infrastructure, transportation, and household products. Unfortunately, the current methods of applying epoxy coatings requires high energy, facility costs, as well as associated operational and safety concerns.⁶ For example, to form epoxy-based electrostatic powder coatings, the substrate must be heated and the sprayed powder must be melted for proper surface deposition.⁸

In contrast, cold spray is a single-step, additive manufacturing process that involves the acceleration (300 to 1200 m/s) of micron-sized commercially available powders whose diameter ranges from 5 to 100 μm . The particles are accelerated toward a suitable substrate using high pressure (6.8 bar/100 psi to 69 bar/1000 psi) and sometimes heat via a gas stream (room temperature to 1200 $^{\circ}\text{C}$). Upon impact with the substrate, the particles undergo tremendous plastic deformation before they consolidate into a solid-state coating by means of ballistic impingement.^{9–17} Cold spray has been extensively developed for metal particles (aluminum,^{18, 19} copper,²⁰ and tin²¹) deposited onto metal, plastic, fabric, and composite substrates; however, the properties of polymer particles that would be needed to form a coating on a surface via a spray process have not yet been established.

To date, a limited number of studies have investigated cold spray deposition using commercially available polymer particles.^{22–24} Bush *et al.* used a combined computational and experimental study to map out the cold spray deposition window of commercial high density polyethylene particles, focusing on the effect that particle properties (temperature, impact velocity, and diameter) have on their deposition efficiency.²⁵ Ravi *et al.* deposited ultra-high molecular weight polyethylene onto aluminum and polypropylene substrates but did not report the deposition efficiency.²³ Using a room-temperature cold spray process, Xu and Hutchings²⁶ impacted acid-modified polyolefins particles onto high density polyethylene and aluminum substrates. Unfortunately, very low deposition efficiencies were obtained, less than 4% deposited on the high density polyethylene substrates and there was no (0%) deposition on the aluminum substrates. The commercial polymer particles designed for traditional powder coatings did not readily form coatings, in part due to their high melting temperature (120 $^{\circ}\text{C}$).²⁷ Alhulaifi *et al.* successfully deposited polyethylene powder (53–75 μm diameter and 0.94 g/cm^3 density) onto a 7075-T6 aluminum substrate using air

as the carrier gas and the critical impact velocity was reported to be m/s. However, there was no evidence reported that the polymer particles melted.²⁸ Thus, we suggest that in order to enable efficient cold sprayed coatings, epoxy-containing polymer particles that have a low softening point²⁹ and a low glass transition temperature are needed.

Previously, epoxy resin imbibed polymer particles were prepared via emulsion polymerization³⁰ but the resulting nanoparticles were much smaller than the size of particles used for cold spray technology and they were in an aqueous emulsion polymer dispersion. In contrast, suspension polymerization, a scalable and industrially relevant process has been broadly used to prepare particles in the size range desired for cold spray technology³¹ and the particles can easily be isolated into dry powders. While previous studies have made microparticles containing a solvent and a healing agent, such as diglycidyl ether of bisphenol A (DGEBA),^{32, 33} multimaleimide,³⁴ or dicyclopentadiene³⁵ using a urea-formaldehyde encapsulation method, the particles were only used in self-healing applications. We suggest that a promising approach would be to use suspension polymerization to develop novel particles containing epoxy resin specifically designed for use in an additive manufacturing coating process.

To obtain polymer particles that would enable room-temperature sprayable coatings, we synthesized thermoplastic polymer particles containing epoxy resin, a reactive thermosetting component of commercial two-component systems, swollen into polymethyl methacrylate (PMMA). We hypothesized that if the core of the polymer particles were amorphous with a low glass transition temperature (near or below the operating temperature of the spray process) that particle deposition would be greatly improved and enable a uniform polymer coating using an additive manufacturing process, such as cold spray. DGEBA is one of the most common epoxy resins in industry and a small molecule that can act as a plasticizer in the polymer particle that we expected would decrease the glass transition temperature, elastic modulus, and degree of crystallinity of the particles.³⁶ The encapsulation of a reactive thermosetting component in the thermoplastic PMMA matrix provides the reactivity and high performance of epoxy, as well as the ease of processing via cold spray. After the particles were well characterized (i.e., chemistry, morphology, and glass transition temperature), their formula was optimized for scale-up so that coating formation could be evaluated using in-house methods. Employing our novel epoxy particles will result in several improvements over the current generation of industrial coatings: (1) the coating procedure is environmentally benign as there are no VOCs, (2) we eliminate the need for the capital associated with solvent remediation, (3) our particles uniquely have an unlimited shelf-life because they only react on impact and thus, (4) complex mixing or plural component spray equipment is avoided. This work explores the feasibility of synthesizing polymer particles containing thermosetting reactive components that could be applied as coatings via cold spray and other powder coating technologies.

MATERIALS AND METHODS

Materials and Chemicals.

The diglycidyl ether of bisphenol A (DGEBA, epoxide equivalent weight 172–176), polyvinyl alcohol (PVA-13k, average M_w 13,000–23,000, 87–89% hydrolyzed), polyvinyl

alcohol (PVA-146k, average Mw 146,000–186,000, 87–89% hydrolyzed), and aluminum oxide (activated, basic, Brockmann I) were purchased from Sigma-Aldrich (St. Louis, MO). Methyl methacrylate (MMA, 98 %, Stabilized/Certified ACS) which was used as the monomer for producing the thermoplastic carrier was obtained from Fisher Chemical (Fair Lawn, NJ). The initiator, benzoyl peroxide (BPO, 75% remainder water), and chloroform-d (99.8% atom D) was purchased from ACROS Organics (Morris Plains, NJ).

Synthesis of Particles via Suspension Polymerization.

Suspension polymerization was used to synthesize the reactive particles (Scheme 1). The initiator and monomer for producing the thermoplastic carrier are typically hydrophobic so that their mixture will disperse as micro-scale droplets in aqueous solution due to vigorous agitation. Each droplet acts as an isolated micro-scale batch. Thus, the monomers polymerize and form polymer particles. Because DGEBA is hydrophobic, we were able to pre-mix the DGEBA in the monomer and initiator mixture before feeding it into the reactor to obtain particles containing DGEBA.

The dispersing agent PVA-13k was dissolved into DI water in a 250 mL glass round-bottom flask equipped with a condenser circulating cooling water and a magnetic stir bar (1000 rpm) at room temperature. After the inhibitor was removed by aluminum oxide, MMA was mixed with BPO and DGEBA until the mixture was homogenous, and then poured into the flask. The reaction was purged using nitrogen. The emulsion was stirred at 1000 rpm for 5 min at room temperature, and then at 650 rpm for 3 h at 70 °C, before being cooled back to room temperature. The particle products were passed through a Buchner filter and dried in a convection oven at 50 °C. The experimental formulations are summarized in Table 1.

The DGEBA:MMA (wt:wt) ratio 12:20 was scaled-up to make the particles LD:LM 12:20 (Table 1) using an ACE 1 L all-in-one benchtop reactor. In a 1 L glass cylindrical flask, the dispersing agent PVA-146k was dissolved in DI water at room temperature under agitation (300 rpm). The flask was equipped with a condenser circulating cooling water, a temperature system, overhead glass stirring assembly with a variable speed motor and controller, and a glass baffle. After the inhibitor was removed using aluminum oxide, MMA was mixed with BPO and DGEBA until the mixture was homogenous, before being poured into the flask. The reaction was purged using nitrogen. The emulsion was stirred at 300 rpm for 30 min at room temperature. The settings were adjusted to 70 °C and 150 rpm and was maintained for 3 h, before being cooled to room temperature. The particle products were passed through a Buchner filter (1 L) and dried in a convection oven at 50 °C.

Chemical and Morphological Characterization of Particles.

Nuclear magnetic resonance (^1H NMR) experiments were performed using a Bruker Avance-III 400 MHz NMR spectrometer using chloroform-d as the solvent. The weight average molecular weight of the particles was measured using an Agilent 1260 Infinity gel permeation chromatography (GPC) system using tetrahydrofuran as the solvent. Thermogravimetric analysis (TGA) was conducted using a TA Instruments TGA Q50. The synthesized particles were heated from 25 °C to 600 °C at a rate of 10 °C/min in a nitrogen environment with 40 mL/min of balance nitrogen purge flow and 60 mL/min of sample

purge flow. The glass transition temperature (T_g) was determined using TA Instruments differential scanning calorimetry (DSC) Q200 with a nitrogen flow rate of 50 mL/min. The synthesized particles were encapsulated in a TA Instruments Standard Aluminum Hermetic Pans and placed in the calorimeter, equilibrated at $-40\text{ }^{\circ}\text{C}$, heated to $100\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$, cooled to $-40\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and heated to $100\text{ }^{\circ}\text{C}$ at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$. For the identification of melting and crystallization, the upper temperature limit was set at $200\text{ }^{\circ}\text{C}$.

To determine the morphology of the particles, SEM was employed (FEI Magellan 400 XHR). Particles were sputter coated for 30 s with gold using a Cressington Scientific Instruments Sputter Coater 108 before imaging. The particles and the interface between the polymer coatings and substrates were imaged using Zeiss Microscope Axio Imager A2M (Thornwood, NY) at $20\times$ magnification and reflected-light bright field. The particles were also imaged using Nikon A1 Point Scanning Confocal fitted with transmitted light detector with a 488 nm imaging laser. The particles size distribution of $n=475$ random particles (LD:LM 12:20) was analyzed using NIS Elements General Analysis.

Evaluation of Particles via Room-Temperature Particle Adherence Tests and Low-Velocity Powder Coating Experiments.

High-speed single particle impact experiment using particles synthesized at various DGEBA:MMA ratios, including LD:LM 12:20, D:M 20:20, and D:M 20:12, whose diameters ranged from $18\text{--}48\text{ }\mu\text{m}$, was conducted using a laser induced projectile impact test (LIPIT, Figure S1) as described previously.³⁷ Briefly, at room temperature, a particle was projected toward an aluminum substrate (commercial polished Al 6061) using a high-energy laser and the movement was recorded by an ultra-fast imaging system, a combination of a femtosecond laser, three electro-optical modulators and a microscope camera. The particle speed ranged from 92 to 669 m/s.

A low-velocity electrostatic powder coating machine (Grizzly T25100, Bellingham, WA) with a nozzle diameter of 1.9 cm, an applied voltage (12 kV), and compressed air at 206 kPa was also tested. Deposition efficiency was evaluated as a function of temperature ($160\text{--}280\text{ }^{\circ}\text{C}$) by spraying 0.3 g of particles (LD:LM 12:20) towards a pre-heated aluminum plate ($5\text{ cm} \times 5\text{ cm}$) that was wrapped with aluminum foil and held at a fixed separation distance (5 cm) from the nozzle.

RESULTS AND DISCUSSION

Chemical, Morphological, and Thermal Characteristics of DGEBA-PMMA Particles

In this study, PMMA was employed as a thermoplastic matrix polymer and DGEBA was employed as the plasticizing monomer to control the glass transition temperature of the particles. DGEBA, MMA, and initiator were pre-mixed and dispersed in water containing a dispersing agent; the MMA in the suspending droplets polymerized and thus, encapsulated DGEBA in the resulting particles, which were successfully synthesized using an in-house built suspension polymerization reactor. Figure 1 shows the nuclear magnetic resonance (^1H NMR) data obtained from DGEBA-PMMA particles synthesized using a weight ratio of 12

to 20. The ^1H NMR signals of the benzoyl group were detected because the benzoyl peroxide (BPO) acts as a hydrophobic catalyst that was encapsulated with DGEBA in the PMMA particles. Both BPO residue and its decomposed products displayed characteristic NMR signals. The DGEBA concentration within the particles was calculated using the peaks of the $\text{CH}_2\text{-O}$ protons on the glycidyl group of DGEBA (4.10 ppm), $\text{CH}_3\text{-O}$ protons of PMMA (3.53 ppm), and aromatic protons of the benzoyl group (8.02, 7.60, 7.45 ppm), see Table S1.

The spectra display the feasibility and success of encapsulating DGEBA into the PMMA particles via our suspension polymerization process; interestingly, the output DGEBA concentration was slightly higher than the input, as summarized in Table S1. That may result from the partial solubility of MMA in water (15 g/L at 20 °C)³⁸ and the insolubility of DGEBA in water (0.7 mg/L at 25 °C)³⁹. The loss of MMA in the droplets increased the DGEBA concentration in the resulting DGEBA-PMMA particles. Our results are not surprising given that Kim *et al.* also reported the change of montmorillonite concentration in PMMA hybrid particles that were synthesized using suspension polymerization.⁴⁰

Thermogravimetric analysis (TGA) was also used to verify the encapsulation of DGEBA in the PMMA particles. The particles prepared with DGEBA:MMA ratios of 8:20 and 12:20 displayed two peaks in the plot of derivative weight versus temperature, Figure 2. The low-temperature peak (at ~280 °C) has the same trend as DGEBA evaporation.⁴¹ This indicates the presence of DGEBA in the particles and that the PMMA degraded at a much higher temperature.

Glassy DGEBA-PMMA particles were produced using suspension polymerization with a DGEBA concentration below 40 wt% and imaged using optical and scanning electron microscopy (SEM) (Figure 3). The particles were spherical, white, hard, and free-flowing. Whereas when the DGEBA concentration was above 40 wt%, the particles were soft and viscous (Figure S3), they agglomerated and even coalesced after the aqueous polyvinyl alcohol solution was filtered out. The glass transition temperature's (T_g 's) of the resulting DGEBA-PMMA particles (Figure 4a) were measured using differential scanning calorimetry (DSC). The encapsulation of DGEBA decreased the T_g of the particles regardless of the final molecular weight of PMMA (Table S2), while DGEBA's role as a plasticizer made the particles softer and stickier by lowering the particles T_g and increasing the viscosity of the formed particles. In addition, higher concentrations of DGEBA increased the particles propensity to stick to each other, and visually, increased the interface area between particles. In terms of storage, transportation, and operation, particles with a high T_g and low DGEBA concentration have significant issues. However, having a T_g below room temperature makes the particles soft and holds potential in additive manufacturing processes (i.e., cold spray) because soft particles can easily deform and coalesce on a substrate.

Thermal and Size Characteristics of DGEBA-PMMA Particles Synthesized in a Large-Scale Suspension Polymerization Reactor

Based on these observations, the DGEBA-PMMA particles prepared using a 12:20 ratio were optimized for a scaled-up synthesis. After scaling, the DGEBA-PMMA particles (Figure 4b) were free-flowing with a T_g of 20 °C and the glass transition process ranged

from 7 °C to 38 °C. In addition, no melting and/or crystallization was detected by DSC below 200 °C. Because the melting point of PMMA is 160 °C, which is far below 200 °C, the DGEBA-PMMA particles have little-to-no partial crystallization, which can promote the coalescence and bonding between particles. Therefore, the particles prepared using a DGEBA:MMA ratio of 12:20 was selected for further characterization and evaluation via a low-speed powder coating technology and a high-speed particle adherence process.

The particle size distribution of the DGEBA:MMA particles prepared using the 1 L reactor (Figure 5) was determined by analyzing 475 random particles scanned using a laser scanning confocal microscope. The particle diameter was $44 \pm 44 \mu\text{m}$ by number average and $154 \pm 50 \mu\text{m}$ by volume average. The number distribution of particles was concentrated below 80 μm and accounted for 82% of all particles. Notably, 93% of the volume of all particles had diameters that were greater than 80 μm in diameter, which is desirable for additive manufacturing applications.

Evaluation of Single DGEBA-PMMA Particle Adherence to Aluminum Substrates at Room Temperature

The deformation of particles prepared at various DGEBA to MMA ratios (12:20, 20:20, and 20:12) upon impact with aluminum substrates was evaluated using laser induced projectile impact tests (LIPIT, Figure S1).^{37, 42} The LIPIT experiments were conducted at room temperature and notably, neither the particles nor the substrate was heated. The T_g of the particles decreased with an increasing DGEBA concentration, which influenced the LIPIT results. The particles rebounded from the substrate if their impact speed was too low. The rebound speed decreased with the impact speed increasing linearly until a critical velocity was obtained, above which the particles adhered to the substrate. The critical velocity necessary for the DGEBA-PMMA particles with a T_g near and below room temperature to adhere are displayed on Figure 6a and Table 2. When the T_g was above 0 °C, the particles required a relatively higher critical velocity, above 400 m/s, while the particles with a T_g below 0 °C adhered to the substrate at a relatively lower critical velocity, below 300 m/s. This difference in critical velocity may be explained by the particle behavior upon impact which was studied through the morphology of the particles once they adhered to the aluminum substrate (Figure 6c). With a T_g of 20 °C, the particles were glassy at room temperature, and thus, they bonded by high kinetic energy (high speed) and cracked upon high-speed impact. With a T_g of 5 °C, the particles were soft, but the elasticity of the particles dominated over their viscosity. As a result, the particles recovered from the deformation induced by the impact and showed a smooth surface and a clean edge. Thus, if the particles had a good elasticity, they required a high kinetic energy (high speed) to bond with the substrate. When the T_g of the particles was decreased to -3 °C, the particles were more viscous than elastic and thus, a portion of the particle's interior flowed out and around the particles post-impact. The soft and viscous particles led to a low critical velocity (below 300 m/s). And the extruding/flow behavior will likely contribute positively to the particles coalescence and film formation during cold spray. To enable the polymer particles to form coatings at room temperature, the T_g should be lower than room temperature and sufficiently low enough to effectively decrease the particle elasticity until the viscosity dominates over their elasticity.

Evaluation of the Adherence of DGEBA-PMMA Particles to Aluminum Substrates via Low-Speed Electrostatic Powder Spray Coating

In addition to the decreasing particle T_g , increasing the temperature of the substrate could also enhance the adhesion behavior between the particles and the substrate. An electrostatic powder spray system was used to perform a low-velocity coating process on an aluminum substrate. Below 160 °C, no particles adherence was observed, while at 160 °C or above, the deposition efficiency increased positively with the temperature of the substrate. The use of voltage (12 kV) yielded a significant improvement and a 70% deposition efficiency on a surface that was preheated to 220 °C (Figure 7). In the 12 kV electric field, the particles, charged positively at the nozzle of the spray gun, were attracted by an electrostatic force perpendicularly toward the surface of substrate that was negatively charged. This extra driving force pushed the particles, increased the contact surface between particles and substrate, and finally enhanced their coalescence. Our 70% deposition efficiency is noteworthy; previously reported deposition efficiencies of particle particles included 0 and 4%.²⁶

The interface between the coating and substrate were imaged using optical microscopy (Figure 8). Due to flattened particle shape and conformal contact to a substrate without air voids, the observed straight-line texture resulted from the surface of the substrate and is indicative of well-bonded particles and strong adhesion. When the temperature of the substrate was increased, the adherent surface area increased. At 200 °C or above, continuous straight-line texture extended across the coating area of multiple particles demonstrating coalescing behavior between particles. The polymer coalescence promoted the adherence between particles and the substrate,²⁶ which aided in the dramatic improvement of deposition efficiency (Figure 8).

Due to the air flow that occurs while powder spraying, the temperature at the surface of the substrate decreased significantly,²⁶ which stopped any further coalescence and yielded uncoated voids at the interface. Supplying sufficient energy via pre-heating a substrate to 280 °C, resulted in a fully coated substrate (Figure 8). When a powder spraying process is conducted industrially using a two-component system, an exothermic reaction between the components initiates a very high temperature that releases a significant amount of energy capable of maintaining an elevated temperature at the surface of the substrate. Thus, industrially, the voids that we observed would likely be eliminated without increasing the temperature of the substrate. Additionally, once the reaction is initiated and is propagating on a surface, the coating process may not require continuous heating because of the high energy released from the coating reaction. Thus, potentially, the voids that we observed at the lower substrate temperatures would not appear in an industrial setting because particle coalescence on the substrate would continue due to heat generation.

The effect of elevated substrate temperature on the coating was evaluated using TGA, DSC, and ¹H NMR. Figure 9 shows the weight loss of the DGEBA-PMMA particles and coatings prepared by electrostatic powder spraying over a temperature ramp. A small weight loss starting at 129 °C was observed in the TGA data acquired on DGEBA-PMMA particles (12:20) prepared in the 1 L reactor (before coating using electrostatic powder spray technology). But, that weight loss was not present in the data after coating. Accordingly, the

^1H NMR signal of the benzoyl was not present after the coating was prepared. The encapsulated BPO residue may have evaporated from the decomposed products. The composition changes are summarized in Table S3, given the assumption that the PMMA was fully deposited in the coatings and that it did not degrade. In terms of coatings prepared on substrates with temperatures between 160 °C and 220 °C, the total weight loss was about 2% and the DGEBA loss was about 2%. Interestingly, the DGEBA concentration in the particles did not change by the DGEBA loss because benzoyl loss also reduced the total mass of the coatings. However, when the temperature was elevated to 280 °C, the DGEBA loss became more significant. We conclude that maintaining the substrate temperature below 220 °C is appropriate for creating coatings from polymer particles with a T_g of 20 °C using a low-velocity powder coating.

CONCLUSION

DGEBA-PMMA particles with various compositions were synthesized via suspension polymerization with well-controlled DGEBA concentrations. The increased encapsulation of DGEBA decreased the T_g 's of the resulting particles. Based on ease of storage, transportation, operation, and processing, particles with a DGEBA:MMA ratio of 12:20 were scaled up for coating evaluation. The resulting particles with a ~40 wt% DGEBA exhibited a T_g of 20 °C and a glass transition temperature that ranged from 7 °C to 38 °C. High-speed single particle impact experiments and low-speed powder coating tests were used to characterize the effect of particle velocity and substrate temperature on coating formation. At room temperature, the adherence of the particles on an aluminum substrate occurred at or above 438 m/s, which is within the range of the typical velocity (300 to 1200 m/s) employed during current cold spray processing. For the particles with a low T_g of -3 °C, the critical velocity decreased to 296 m/s. Low-speed particles adhered to aluminum substrate at or above 160 °C whereas when higher substrate temperatures were tested (above 200 °C) the deposition efficiency reached ~70% with great particle coalescence and minimal material losses. This study demonstrates that reactive polymer particles with T_g 's below room temperature can be used as the main component in multiple additive manufacturing processes that feature low velocity and/or a low temperature deposition process.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.

Schematic overview of the suspension polymerization process used to synthesize DGEBA-PMMA particles.

Figure 1.

^1H NMR data obtained from DGEBA-PMMA particles containing 37.3 wt% DGEBA. ^1H NMR (400 MHz, CDCl_3 , δ): DGEBA 7.06 (d, $J = 8.6$ Hz, 4H), 6.75 (d, $J = 8.6$ Hz, 4H), 4.10 (dd, $J = 11.0, 3.3$ Hz, 2H), 3.88 (dd, $J = 11.0, 5.5$ Hz, 2H), 3.27 (m, 2H), 2.83 (t, $J = 4.5$ Hz, 2H), 2.67 (dd, $J = 4.8, 2.6$ Hz, 2H), 1.56 (s, 6H); PMMA 3.53 (s, 3H), 2.00–1.15 (m, 2H), 0.95 (s, 1H), 0.78 (s, 1H), 0.77 (s, 1H); Benzoyl group 8.02 (d, $J = 8.4$ Hz, 2H), 7.60 (t, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 2H). For reference, Figure S2 compares the ^1H NMR DGEBA-PMMA particle data to PMMA and DGEBA.

Figure 2. Derivative weight of DGEBA-PMMA particles prepared from various DGEBA:MMA weight ratios as a function of temperature. DGEBA evaporated in TGA is provided as a control.

Figure 3. Representative (A) optical and (B) SEM micrograph of DGEBA-PMMA particles. Representative particles were fabricated using a DGEBA:MMA ratio of 12:20 (37.3 wt% DGEBA).

Figure 4. (A) Glass transition temperature (T_g) as a function of DGEBA concentration for DGEBA-PMMA particles. (B) DSC heat flow as a function of temperature for particles. Data collected on particles prepared using a DGEBA:MMA ratio of 12:20 in a 1 L suspension polymerization reactor.

Figure 5. (A) Number and (B) volume distribution of DGEBA-PMMA particles. Data collected on particles prepared using a DGEBA:MMA ratio of 12:20 in a 1 L suspension polymerization reactor.

Figure 6.

Plots and representative images of single particle impact experiments conducted at room temperature. (A) Rebound speed versus impact speed and (B) the coefficient of restitution versus impact speed for DGEBA-PMMA particles. Data collected on particles prepared using a DGEBA:MMA ratio of 12:20* (green, $T_g = 20$ °C), 20:20 (blue, $T_g = 5$ °C), and 20:12 (red, $T_g = -3$ °C). The size of the symbols are relative to the particle size (diameters ranging from 18–48 μm). (C) Optical micrographs of particles prepared from DGEBA:MMA ratios of 12:20*, 20:20, and 20:12 after impacting the aluminum substrate. Particle ratios with an (*) asterisk indicate that they were prepared using the larger, 1 L suspension polymerization reactor.

Figure 7.

An electrostatic powder spray system was used to determine the deposition efficiency of DGEBA-PMMA particles with and without voltage as a function of substrate temperature. Data collected on particles prepared using a DGEBA:MMA ratio of 12:20 in a 1 L suspension polymerization reactor.

Figure 8.

Optical micrographs of the interface between the polymer coatings and the aluminum substrate after electrostatic powder spraying with voltage (12 kV) as a function of substrate temperature. A schematic is provided that depicts the cross-section of particles adhered to the substrate. Data collected on particles prepared using a DGEBA:MMA ratio of 12:20 in a 1 L suspension polymerization reactor.

Figure 9.

TGA provides the weight loss over a temperature ramp of coatings prepared by electrostatic powder spraying. Coatings were prepared from DGEBA-PMMA particles as a function of substrate temperature, 160 °C (red dashed line), 220 °C (blue dotted line), and DGEBA (no MMA, pink dot-dashed line). DGEBA-PMMA particles (not coatings) are provided as a control (solid black line). Particles were prepared using a DGEBA:MMA ratio of 12:20 in a 1 L suspension polymerization reactor.

Table 1.

Formula of DGEBA:MMA particles that were synthesized in a small-scale and large-scale suspension polymerization reactor.

	Small									Large
DGEBA:MMA	D:M	D:M	D:M	D:M	D:M	D:M	D:M	D:M	D:M	LD:LM
[wt:wt]	<u>1:20</u>	<u>2:20</u>	<u>4:20</u>	<u>8:20</u>	<u>12:20</u>	<u>16:20</u>	<u>20:20</u>	<u>20:16</u>	<u>20:12</u>	<u>12:20</u>
MMA	16.0	16.0	16.0	16.0	16.0	16.0	16.0	12.8	9.6	80
BPO	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	2
PVA	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	8
DI water	80	80	80	80	80	80	80	80	80	800
DGEBA	0.8	1.6	3.2	6.4	9.6	12.8	16.0	16.0	16.0	48

Table 2.

Properties of DGEBA-PMMA particles determined by single particle impact experiments conducted at room temperature.

DGEBA:MMA ratio	DGEBA	Concentration	T_g [°C]	Critical Velocity [m s ⁻¹]
	[wt%]			
12:20 *	37		20	438
20:20	52		5	487
20:12	64		-3	296

* Particles were prepared using a 1 L suspension polymerization reactor.