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A method for rubber toughening powder coatings

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Abstract

This paper describes a new method for rubber toughening brittle powder coatings. The design involves the use of toughening agents with specific physical and chemical properties. The modifiers are low-to-medium molecular weight polymers with polymerizable end groups (macromonomers). To achieve the physical properties required for fabrication into fine powders for subsequent deposition using conventional powder coating equipment, semi-crystalline polymers with T_g's well below room temperature and melting points above ~ 70 °C were required. Upon copolymerization with a thermosetting resin, crystallization of the modifier was precluded provided that low ethylene oxide compositions were employed. This scheme, in principle, yields an amorphous low T_g modifier chemically bound to the cured network. Poly(ethylene oxide), PEO, was found to be an excellent candidate, since it has a T_g of -68°C and a T_m of 70°C, sufficient crystallinity for friability and functional end groups for copolymerization. Free radical polymerization of 2,2-bis[4-vinylbenzoyloxyphenyl] hexafluoropropane and step-growth polymerization of 4,4′-(hexafluoroisopropylidene)diphenyl cyanate were utilized to demonstrate the feasibility of this approach. An electrostatic powder coater was used to co-deposit the PEO macromonomers with either of the thermosetting precursor monomers, followed by thermal curing to produce the modified networks. The resulting networks showed multiphase morphologies with improved toughness.

Introduction

Deposition of polymer films via powder coating processes is a rapidly expanding technology. Powder deposition offers numerous environmental and economic advantages over conventional coating processes including solventless deposition (100% solids), high efficiency deposition (compared to spin coating where 90 – 95% of material is lost), and low melt viscosity for planarization. The requirements for a material to be deposited as a powder generally include brittle mechanical properties for powder formation (friability), a melting or softening point substantially above room temperature for a long shelf life, and a polymerization temperature high enough to provide a processing window to allow for planarization prior to gelation. The two main classes of materials utilized as powder coatings include thermosetting resins (epoxies, polyesters, acrylics, etc.) and thermoplastics (polyamides, polyolefins, etc.) (1,2). Although the thermoplastic materials offer substantially tougher coatings, it is at the expense of the friability required for optimum particle formation/size. Conversely, the thermosetting systems may be readily milled into fine powders, however, the subsequent cured films are brittle and have high residual stress from thermal cycling.

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The incorporation of elastomeric modifiers is often successfully used to enhance the fracture strength of brittle materials. The phase-separated rubber particles are presumed to act as stress concentrating sites, thus initiating energy absorbing "toughening" processes such as crazing and plastic deformation. This technology has been applied to epoxy resins through the utilization of low molecular weight liquid butadiene acrylonitrile copolymers having either carboxyl (CTBN) or amine (ATBN) reactive end groups (3 – 7). Other elastomeric modifiers that have been studied include acrylic elastomers (7), poly(oxypropylene amines) (8) and polysiloxane copolymers (6,7). The K_{IC}, fracture toughness, values of the rubber modified epoxy networks are typically found to be considerably higher than those for the unmodified materials. The processing of such rubber toughened systems involves heating the two components up to the softening point of the thermosetting resin where the thermosetting resin solvates the elastomeric oil to form a homogeneous solution, allowing copolymerization. Upon curing, the increase in the molecular weight due to the crosslinking reaction causes the elastomeric component to phase separate from the thermosetting matrix. The window for phase separation is fairly narrow and must occur early in the polymerization prior to gelation, at which time the morphology is fixed, as described by Gillham (9) in an isothermal time-temperature transformation (TTT) diagram. Unfortunately, the use of this strategy to toughen thermosetting powder coatings is not directly applicable since the low T_g elastomeric oils are not amenable towards electrostatic or electrophotographic powder deposition techniques.

To investigate the possibility of rubber toughening brittle powder coatings while maintaining friability, semi-crystalline polymers with functional (polymerizable) end groups, T_g's below room temperature and T_m's above 70 °C were used as modifiers. Copolymerization of the thermosetting resin with relatively low levels of the semi-crystalline macromonomer should preclude the crystallization of the modifier, thus yielding a low T_g elastomeric phase if phase separation can be induced. A semi-crystalline modifier possessing adequate crystallinity should be sufficiently friable for powder formation and deposition. Poly(ethylene oxide), PEO, was found to be an excellent candidate, since it has a T_g of – 60 °C, a melting point of 70 °C, and has sufficient crystallinity for friability or powder formation. In addition, poly(ethylene oxide) is available with a variety of monofunctional, polymerizable end groups. In this article the use of poly(ethylene oxide) macromonomers to co-deposit in powder form and toughen two brittle thermosetting resins will be described.

Experimental

Materials

2,2-Bis[4-vinylbenzyloxyphenyl]hexafluoropropane, styrenic resin, was prepared according to a literature procedure (10). Monofunctional poly(ethylene oxide) oligomers (Polysciences) with mono-hydroxyl and methacrylate termination were used as received. The 4,4'-(hexafluoroisopropylidene)diphenylcyanate, dicyanate resin, was purchased from Rhone-Poulene and was used as received.

Powder formation and size classification

The styrenic resin milled to a fine powder, 33.2 μm particle size, but there was some caking inside the mill. The caking reduced the yield of powder, but did not affect the performance of the powder. This problem was minimized by cooling the mill. The tribocharge was + 4.2 μC/g. A recrystallized portion of this materialized was found to mill to a finer powder, 15.7 μm particle size, but there was still some caking in the mill. Polyethylene oxide (MW 4000) milled very well (some small amount of caking) and the powder charged to + 2.4 μC/g.

Sample preparation

The modification of the styrenic resin was accomplished by mixing the methacrylate-terminated poly(ethylene oxide) powder with the styrenic powder in an Erlenmeyer flask with a stir bar. The flask was sealed with a rubber septum under an oxygen atmosphere, and placed in an oil bath (135 °C) where the monomer melted and dissolved the oligomer. The modification of cyanate resin was accomplished in an analogous fashion except the initial mixing was in a nitrogen atmosphere. The solutions were then poured into a hot silicone mold (290 °C), sealed and cured (1.5 h). Alternatively, the powders were deposited on a silicon wafer using an electrostatic powder coater (Model C-30 from Electrostatic Technology), and cured at 290 °C for 1.5 hours.

Characterization

Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) of the polymer films was performed at a heating rate of 5 °C/min for the variable temperature scans. Dynamic mechanical behavior was measured using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) in the tension mode with a heating rate of 10 °C/min (10 Hz).

The value of K_{IC} (fracture toughness) indicates the critical stress intensity for a load which will cause catastrophic failure in the tension mode and, in this study, the three-point bend specimen geometry was used. For a three-point bend specimen

$$K_{IC} = \frac{3PLa^{1/2}Y}{Bw^2} \tag{1}$$

where P is the load, w is the width, L is the length (= 2w), B is the thickness, a is the crack length and Y is a geometric factor given by

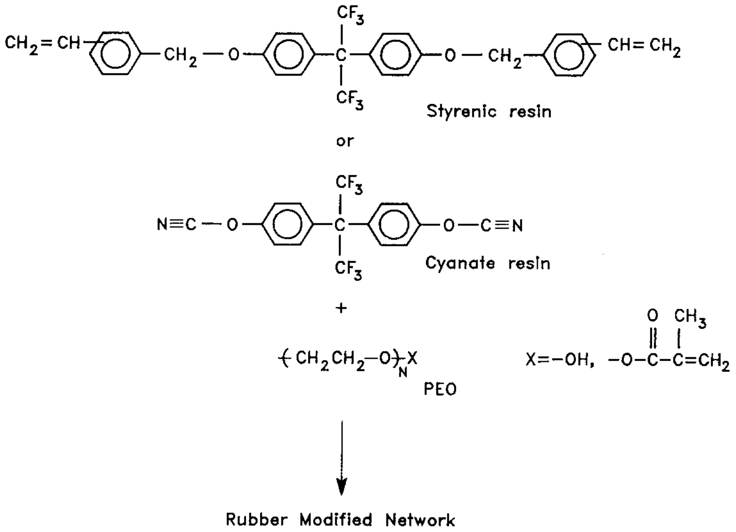
$$Y = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4 . \tag{2}$$

The criteria described in ASTM E399 were followed as closely as possible. The dimensions of the fracture toughness samples were approximately 3.2 × 6.4 × 38.1 mm. The precrack was introduced with a saw cut and then "sharpened" with a new razor blade. The cross-head speed was 0.5 mm/min for all samples tested.

Results and discussion

To demonstrate the feasibility of this new approach to rubber tougher brittle powder coatings, two thermosetting systems, including a styrenic and a cyanate resin, were modified with poly(ethylene oxide), PEO. These thermosetting resins were chosen since they are low molecular weight, crystalline and self-polymerizing monomers which could be readily milled into fine powders. The melting points are between 70 and 80 °C which are high enough above room temperature to allow for extended shelf life, yet provide a sufficient processing window for copolymerization and/or melt flow prior to the onset of gelation. Likewise, the functional PEO could be readily milled into fine powders, provided the molecular weight was above 2,000 g/mol. An electrostatic coater was used to co-deposit the poly(ethylene oxide) with either the styrenic or cyanate resins (Scheme 1).

Both of the thermosetting resins, once melted, solvated the poly(ethylene oxide), forming clear homogeneous solutions.



Scheme 1

McGrath and co-workers (11) have demonstrated that a significant correlation exists between end group functionalization and the resulting morphology, interfacial adhesion between phases, solvent resistance and impact resistance in thermoplastic toughened thermosets. Reactive functional end groups on the thermoplastic enhances compatibilization thus resulting in smaller phases of more uniform size and distribution. These morphologies are usually more desirable when attempting to enhance the fracture toughness properties of a brittle thermoset. For the step growth resin system described in this paper, PEO modified cyanate resin, monofunctional hydroxyl terminated ethylene oxide oligomers of 4,000 and 18,000 g/mol were employed. The reaction of cyanate resins with labile hydrogen compounds, in the presence of a base or with the application of heat, has been described by Grigat and Putter (12). Aryl cyanates react with alcohols, such as hydroxyl terminated PEO, to yield alkyl aryl imidocarbonates (12). The imidocarbonate adduct, however, is thermally reversible at temperatures in excess of 150 °C. Other side reactions are also possible and are described in detail by Grigat and Putter (12). Due to the moderate viscosity of the modified resins, the compositions were maintained at 10 wt.% (Table 1). Conversely, the modification of the styrenic resin required a PEO with free radically polymerizable end groups. The only commercially available material satisfying this criterion was a methacrylate terminated ethylene oxide oligomer of 1,000 g/mol. Since this oligomer was not of sufficient molecular weight to achieve the required level of crystallinity to be milled, high molecular weight PEO (4,000 g/mol) was blended (50% by weight) to increase the friability (Table 1, entry 5). In each case, network formation was achieved by heating the samples to 290 °C (1.5 h).

Upon network formation via step-growth (cyanate resin) or chain-growth (styrenic resin) chemistry as shown in Scheme 1, the PEO modified systems produced clear tough films with no evidence of large scale phase separation. The characteristics of these modified networks are shown in Table 1. Two mono-hydroxyl terminated PEO molecular weight were employed to modify the polycyanurate network, and 4,000 and 18,000 g/mol with PEO compositions of 10 wt.%. The total composition of methacrylate terminated PEO used to modify the styrenic network was maintained at 20 wt.%, with 50% of the PEO, in this case, as a free blend. In all examples, the PEO compositions were low (i.e., at 20 wt.% or below) so as to minimize the possibility of crystallization in the network after cure. The thermal and fracture characteristics of both modified networks are also shown in Table 1.

TABLE 1. Characteristics of Thermosets and Modified Thermosets

Sample Entry	PEO Block Length, g/mol	PEO Composition, wt.%	T_g °C	Polymer Decomposition Temp., °C	$K_{IC}/10^6$ $N/m^{3/2}$
1†	—	—	*	390	0.33
2‡	—	—	304	390	0.38
3	4,000	10	—	350	—
4	18,000	10	230	350	0.47
5	1,000/4,000	20	*	340	0.44

†Styrenic resin; ‡Cyanate resin; *Not detectable by DSC.

The dynamic mechanical behavior for the PEO modified polycyanurate networks prepared through step-growth polymerization are shown in Figure 1. The parent polycyanurate network shows a modulus-temperature profile which is invariant up to T_g (~290 °C), where a small drop in modulus is observed, indicative of a highly crosslinked structure. The PEO modified networks showed markedly different behavior. First, a transition at ~ − 65 °C was observed in the tan δ corresponding to the T_g of the PEO phase. It is important to note that this T_g is nearly identical to that of the parent PEO oligomer and that the modulus drops and then remains constant, indicative of high phase purity of the PEO component. Furthermore, at these low compositions there was no evidence of crystallization of the PEO block. Conversely, the T_g of the high temperature matrix resin is substantially depressed and shows a minimal "rubbery" plateau region (Figure 1). The

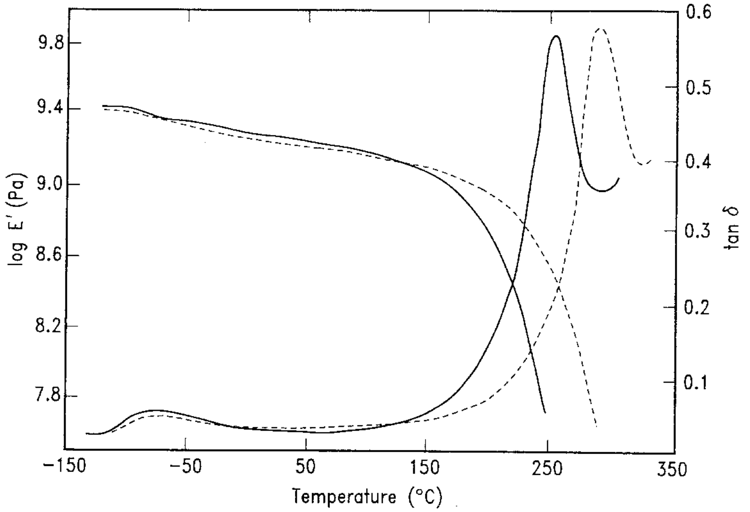


Figure 1. Dynamic mechanical analysis of modified network **3** (——) and **4** (----).

depression of the glass transition temperature is probably due to the formation of a more "lightly" crosslinked network. Incorporation of the monofunctional hydroxyl terminated PEO reduces the crosslink density since cyanate moieties, previously capable of trimerizing with other cyanate groups, are rendered unreactive with the addition of the monofunctional modifier. The phase separated materials were transparent, indicating that the size scale of the phase separation is well below 1 μm.

Figure 2 contains the dynamic mechanical behavior of the PEO modified styrenic network cured by free radical chain polymerization. Two transitions were observed, indicative of a phase separated morphology. The first was at ~ – 50 °C which is nearly identical to that of the oligomer used in the synthesis, indicative of minimal contamination in this phase. Conversely, the T_g of the high temperature component was substantially depressed, consistent with poor phase purity. In this modification scheme unbound PEO was also used as a modifier. In this case we believe that the chemically reacted PEO serves to compatibilize the higher molecular weight unbound PEO to limit the size scale of the phase separation. In fact, SEM analysis of the (cold-snap) fracture surface showed that the sample lacked an observable morphology at magnifications high enough to observe 1000 Å particles (20,000X). This fact, taken together with the optical clarity of the samples and the dynamic mechanical evidence for phase separation, suggests a fine, microphase separated morphology in the hundreds of angstroms size scale.

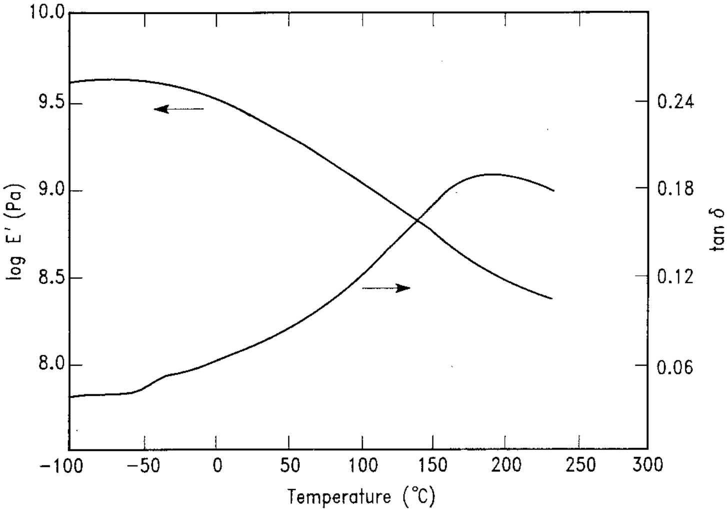


Figure 2. Dynamic mechanical analysis of modified network 5 (——).

The fracture toughness, $K_{I,C}$ values for the PEO modified networks are shown in Table 1 together with the unmodified networks to facilitate comparison. As expected, the incorporation of the elastomeric modifier improved the toughness of both of the resins. The mechanisms of toughening are believed to be similar to those previously reported for other rubber toughened thermosets (5,6).

Summary

A general method for rubber toughening brittle powder coatings has been developed, where the impact modifier is a semi-crystalline polymer with a T_g below room temperature

and a melting point above ~ 70 °C. These materials may be milled and deposited as a conventional powder. Upon copolymerization with a thermosetting resin, crystallinity is precluded, provided the modifier is maintained at compositions below 30 wt.%. For the examples investigated, phase separation morphologies were observed along with the expected improvements in fracture toughness.

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