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(54) **Titre : RESINE EPOXY A MODIFICATION ISOCYANATE NON FRITTEE POUR APPLICATIONS EPOXY RELIEES PAR FUSION**
(54) **Title: NON-SINTERING ISOCYANATE MODIFIED EPOXY RESIN FOR FUSION BONDED EPOXY APPLICATIONS**

(57) **Abrégé/Abstract:**
Thermosetting epoxy-terminated oxazolidinone ring containing polymers which are obtainable by reacting at least one polyisocyanate compound with at least one hydroxy group containing epoxy resin and/or a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups. The polymers have an onset glass transition temperature of at least about 45°C and are capable of showing an onset glass transition temperature in the cured state at least about 160°C. Powder coating compositions comprising these polymers are also disclosed.

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(54) Title: NON-SINTERING ISOCYANATE MODIFIED EPOXY RESIN FOR FUSION BONDED EPOXY APPLICATIONS

(57) Abstract: Thermosetting epoxy-terminated oxazolidinone ring containing polymers which are obtainable by reacting at least one polyisocyanate compound with at least one hydroxy group containing epoxy resin and/or a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups. The polymers have an onset glass transition temperature of at least about 45°C and are capable of showing an onset glass transition temperature in the cured state at least about 160°C. Powder coating compositions comprising these polymers are also disclosed.

NON-SINTERING ISOCYANATE MODIFIED EPOXY RESIN FOR FUSION BONDED EPOXY APPLICATIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to substantially sinter-free isocyanate modified epoxy resins for fusion-bonded epoxy coating applications and to powder coating compositions which comprise these resins. The compositions may be suitable, among other things, for making corrosion protection Fusion-Bonded Epoxy (FBE) coatings or primers for pipelines through which hydrocarbons are transported from production facilities to processing facilities at high temperatures (>110°C).

Discussion of Background Information

As the service temperatures of oil and gas pipelines increase due to the exploitation of ultra deep reservoirs and tar sands, the pipe coating industry has been developing high performance corrosion protection coatings and insulating multilayer systems to meet the industry needs. Currently, the pipe coating industry can provide cost-effective FBE coatings systems to meet the requirements for corrosion protection of pipelines operating at temperatures of up to about 140°C. However, it has been predicted that the next generation of high service temperature pipelines will operate at even higher temperatures. To meet this requirement, the pipe coating industry needs FBE coating or primers systems that are able to protect from corrosion pipelines operating at higher service temperatures. Further, in order to be cost competitive the FBE coating or primer systems must be applicable by using state-of-the-art powder coating technology.

A key ingredient in an FBE coating composition is a Solid Epoxy Resin (SER), which determines the properties of the coating to a high extent. One strongly desirable property of an SER for use in FBE coating applications is an onset glass transition temperature, Tg, which is at least about 45°C, to avoid sintering or fusion of the resin pellets under the hot and humid conditions which are frequently encountered, especially in summer, in non air-conditioned warehouses or during transportation of the resin or the powder coating formulation based thereon.

Once formulated into a powder coating composition, the SER also needs to impart a good balance of physical properties to the FBE coating. One important property of the

finished FBE coating is an onset glass transition temperature that should be higher than the service temperature of the substrate. Another desirable property of the FBE coating is a good adhesion to the substrate.

It has now unexpectedly been found that by using a particular type of epoxy resin and one or more polyisocyanate compounds for making an isocyanate modified epoxy resin, it is possible to produce an SER with an onset glass transition temperature of at least about 45°C which, when incorporated into a powder coating composition, is capable of providing an FBE coating that has an onset glass transition temperature of at least about 160°C.

SUMMARY OF THE INVENTION

The present invention provides thermosetting epoxy-terminated oxazolidinone ring containing polymers which are obtainable by reacting at (a1) at least one (preferably liquid) hydroxy group containing epoxy resin and/or (a2) a combination of at least one epoxy resin (e.g., a hydroxyl group containing resin or a resin which comprises no or only very few hydroxy groups) and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups with (b) at least one polyisocyanate compound in the presence of (c) at least one catalyst which is capable of promoting the formation of oxazolidinone rings and the branching of the polymers. In an uncured state, these polymers have an onset glass transition temperature of at least about 45°C. Further, in the cured state, these resins are capable of showing an onset glass transition temperature at least about 160°C. The onset glass transition temperature can be determined, for example, by Differential Scanning Calorimetry (DSC).

In one aspect of the instant polymers, the at least one polyisocyanate compound may comprise polymeric MDI (polymeric 4,4'-methylene bis(phenylisocyanate)) or a blend of toluene diisocyanate (TDI) and polymeric MDI. For example, the weight ratio of polymeric MDI to TDI may be from about 10:90 to about 90:10.

In another aspect of the instant polymers, the at least one hydroxy group-containing epoxy resin may comprise a hydroxy group-containing diglycidyl ether. For example, at least about 10% (and preferably at least about 20%) of the diglycidyl ether molecules may be hydroxy group-containing oligomers.

In another aspect of the instant polymers, (a1) may comprise diglycidyl ether of bisphenol A.

In another aspect, the weight ratio (a1):(b) may be from about 75:25 to about 85:15. For example, it may be from about 77:23 to about 81:19, e.g., from about 78:22 to about 80:20.

The instant polymers also comprise at least one catalyst (c) such as, e.g., an imidazole, like 2-phenyl-imidazole, preferably in a concentration of from about 100 to about 2000 ppm, based on the total polymer.

In yet another aspect of the polymers of the present invention, the (molar) ratio of oxazolidinone rings to isocyanurate rings in the polymers may be from about 95:5 to about 100:0 and/or the polymers may have an epoxy equivalent weight of at least about 400 eq/gr.

In an embodiment, there is provided a thermosetting epoxy-terminated oxazolidinone ring containing polymer, wherein the polymer is obtained by reacting at least one of (a1) at least one hydroxy group containing epoxy resin comprising bisphenol A diglycidyl ether and (a2) a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that forms crosslinks between epoxy groups with (b) at least one polyisocyanate compound selected from the group consisting of polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI) and a mixture of polymeric MDI and toluene diisocyanate (TDI) with the proviso that when said polyisocyanate comprises a mixture of polymeric MDI and TDI, the mixture comprises at least 20 percent by weight of said polymeric MDI; in the presence of (c) at least one catalyst which promotes a formation of oxazolidinone rings and a branching of the polymer and wherein the polymer in an uncured state has an onset glass transition temperature of at least 45°C and is capable of showing an onset glass transition temperature in a cured state of at least 160°C, wherein the weight ratio of said bisphenol A diglycidyl ether and the at least one polyisocyanate compound is from about 77:23 to about 81:19, and wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer has an epoxy equivalent weight of at least 400, and wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer is a powder coating composition suitable for producing fusion–bonded epoxy coating.

In a still further aspect of the instant polymers, these polymers may be suitable for use in powder coating compositions for producing fusion-bonded epoxy (FBE) coatings.

The present invention also provides thermosetting powder coating compositions which comprise (a) one or more thermosetting polymers according to the present invention as set forth above (including the various aspects thereof) and (b) one or more curing catalysts for the thermosetting polymer(s).

In one aspect, these compositions may comprise from about 10% to about 99% by weight of (a), based on the total weight of the composition.

The present invention also provides a method for providing a substrate with a fusion-bonded epoxy (FBE) coating or primer and a substrate that has been coated by this method. The method comprises subjecting the substrate to a powder-coating process with the powder-coating composition according to the present invention as set forth herein.

In one aspect of the method, the substrate may comprise a metal (e.g., steel) substrate and/or the substrate may comprise a pipe.

The present invention also provides a substrate that carries thereon a fusion-bonded epoxy coating made from the powder-coating composition according to the present invention as set forth herein.

In one aspect of the substrate, the fusion-bonded epoxy coating thereon may have an onset glass transition temperature at least about 160°C.

The present invention also provides a method of making an epoxy-terminated oxazolidinone ring containing polymer which has an onset glass transition temperature in the uncured state of at least about 45°C and is capable of showing an onset glass transition temperature of at least about 160°C in the cured state. The method comprises the addition of at least one polyisocyanate compound (for example, a blend of polyisocyanate compounds,

which preferably comprise toluene diisocyanate (TDI) and polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI)) to a mixture of (a1) at least one (preferably liquid) hydroxy group-containing epoxy resin and/or (a2) a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups and (b) at least one compound that is capable of catalyzing the reaction between epoxy groups and isocyanate groups. The addition is carried out under conditions (for example, at a rate and at a temperature) which favor the formation of oxazolidinone rings over the formation of isocyanurate rings. Upon completion of the addition the resultant mixture is kept at an elevated temperature for a time which is sufficient to afford an epoxy-terminated oxazolidinone ring containing polymer which has an onset glass transition temperature of at least about 45°C.

In one aspect of the method, the addition of the at least one polyisocyanate compound may be carried out in two or more steps. For example, the TDI and the polymeric MDI may be added separately and/or a mixture of TDI and polymeric MDI may be added.

In another aspect, the addition may be carried out at a temperature of at least about 150°C, e.g., at least about 155°C or at least about 160°C.

In yet another aspect of the instant method, the elevated holding temperature may be at least about 160°C.

In a still further aspect, the at least one epoxy resin may comprise a hydroxy group containing bisphenol A diglycidyl ether. For example, at least about 10% (and preferably at least about 20%) of the diglycidyl ether molecules may be hydroxy group-containing oligomers.

In another aspect, the weight ratio of polymeric MDI to TDI may be from about 10:90 to about 90:10 and/or the produced polymer may have an epoxy equivalent weight of at least about 400.

In an embodiment, there is provided a method of making an epoxy-terminated oxazolidinone ring containing polymer which has an onset glass transition temperature in an uncured state of at least 45°C and is capable of showing an onset glass transition temperature of up to about 160°C in a cured state, wherein the method comprises (i) adding, under conditions which favor a formation of oxazolidinone rings over a formation of isocyanurate rings, at least one polyisocyanate compound selected from the group consisting of polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI) and a mixture of polymeric MDI and toluene diisocyanate (TDI) with the proviso that when said polyisocyanate comprises a mixture of MDI and TDI, the mixture comprises at least 20 percent by weight of said polymeric MDI to a mixture of (a1) at least one hydroxy group containing epoxy resin comprising bisphenol A diglycidyl ether and/or (a2) a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups and (b) at least one compound which is capable of catalyzing a reaction between epoxy groups and isocyanate groups and is capable of promoting a branching of the polymer; and (ii) upon completion of the addition according to (i), keeping a resultant mixture at an elevated temperature for a time which is sufficient for an epoxy-terminated oxazolidinone ring containing polymer to branch in the presence of (b) and to afford an onset glass transition temperature of the uncured polymer of at least 45°C, thereby producing said epoxy-terminated oxazolidinone ring containing polymer having an epoxy equivalent weight of at least 400, wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer is a powder coating composition suitable for producing fusion-bonded epoxy coating, and wherein the weight ratio of said bisphenol A diglycidyl ether and the at least one polyisocyanate compound is from about 77:23 to about 81:19.

The present invention also provides a polymer which has been made by the process according to the present invention as set forth herein (including the various aspects thereof).

Other features and advantages of the present invention will be set forth in the description of the invention that follows, and will be apparent, in part, from the description or may be learned by practice of the invention. The invention will be realized and attained by the compositions, products, and methods particularly pointed out in the written description and claims hereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is further described in the detailed description which follows, in reference to the drawings by way of non-limiting examples of exemplary embodiments of the present invention, wherein:

Figure 1 represents a DSC thermogram for determining the onset glass transition temperature of the polymer of Example 6 below;

Figure 2 represents a DSC thermogram for determining the onset glass transition temperature of the cured powder coating composition of Example 12 below;

Figure 3 represents a DSC thermogram for determining the onset glass transition temperature of the FBE coating made from the powder coating composition of Example 12 below;

Figure 4 represents a graph that shows the polymer EEW and the polymer onset glass transition temperature as a function of the digestion time for the polymer of Example 7b below;

Figure 5 represents a graph that shows the polymer onset glass transition temperature as a function of the polymer Epoxy Equivalent Weight (EEW) for the polymer of Example 7b below;

Figure 6 represents a graph that shows the melt viscosity as a function of the polymer EEW for the polymer of Example 7b below;

Figure 7 represents a graph that shows the polymer EEW and the polymer onset glass transition temperature as a function of the digestion time for the polymer of Example 7c below;

Figure 8 represents a graph that shows the polymer onset glass transition temperature as a function of the polymer EEW for the polymer of Example 7c below;

Figure 9 represents a graph that shows the melt viscosity as a function of the polymer EEW for the polymer of Example 7c below; and

Figure 10 represents a graph that shows the polymer onset glass temperature as a function of the polymer EEW for the polymers of Examples 7b and 7c below.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The thermosetting epoxy-terminated oxazolidinone ring containing polymers of the present invention preferably comprise the reaction product of at least one (preferably, but not limited to, liquid) hydroxy group containing epoxy resin and at least one polyisocyanate compound, or a mixture of two or more polyisocyanate compounds which comprise (e.g.,

may consist of or may consist essentially of) toluene diisocyanate (TDI) and polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI) and a suitable catalyst.

The hydroxy group containing epoxy resin may be a single resin or a mixture of two or more epoxy resins. If more than one epoxy resin is present, at least one of these epoxy resins (and preferably all of them) contain hydroxy groups. By way of non-limiting example, preferably more than about 7%, e.g., at least about 10%, e.g., at least about 15%, or at least about 20% of the molecules of the epoxy resin(s) comprise one or more hydroxy groups.

Non-limiting specific examples of hydroxy group containing epoxy resins which may be used for the production of the thermosetting isocyanate modified epoxy-terminated polymers of the present invention include diglycidyl ethers of diols such as, e.g., bisphenol A, brominated bisphenol A, bisphenol F, bisphenol K (4,4'-dihydroxybenzophenone), bisphenol S (4,4'-dihydroxyphenyl sulfone), hydroquinone, resorcinol, 1,1-cyclohexanebisphenol, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, butanediol, hexanediol, cyclohexanediol, 1,4-bis(hydroxymethyl)benzene, 1,3-bis(hydroxymethyl)benzene, 1,4-bis(hydroxymethyl)cyclohexane and 1,3-bis(hydroxymethyl)cyclohexane; diglycidyl esters of dicarboxylic acids such as, e.g., hexahydrophthalic acid; diepoxy compounds such as, e.g., cyclooctene diepoxide, divinylbenzene diepoxide, 1,7-octadiene diepoxide, 1,3-butadiene diepoxide, 1,5-hexadiene diepoxide and the diepoxide of 4-cyclohexenecarboxylate 4-cyclohexenylmethyl ester; and glycidyl ether derivatives of novolacs such as phenol novolac, cresol novolac and bisphenol A novolac. Mixtures of two or more of these epoxy resins may be used as well.

A preferred example of an epoxy resin for use in the present invention includes a hydroxy group-containing diglycidyl ether of a bisphenol such as, e.g., bisphenol A. It is particularly preferred if at least about 20%, e.g., at least about 50%, at least about 70%, at least about 80%, or at least about 90% by weight (e.g., about 100%), of all epoxy resins used for the production of the polymer of the present invention comprise diglycidyl ethers of one or more bisphenols such as, e.g., bisphenol A. The bisphenol (A) diglycidyl ether preferably comprises oligomers (e.g., oligomers produced during the reaction of, e.g., bisphenol A and epichlorohydrin in the presence of alkali) in a proportion such that at least about 10%, preferably at least about 20% of all diglycidyl ether molecules comprise one or more hydroxy groups. The epoxy equivalent weight (EEW, defined herein as the (average) molecular weight divided by the number of epoxy groups per molecule) of the

diglycidylether of bisphenol A may, for example, be at least about 180, but will usually be not higher than about 250, e.g., not higher than about 230, or not higher than about 210.

The preferred isocyanate starting material for the production of the thermosetting resin of the present invention comprises at least two components, i.e., TDI and polymeric MDI. Preferably, the weight ratio polymeric MDI:TDI is at least about 10:90, e.g., at least about 55:45, or at least about 60:40, but will usually be not higher than about 90:10. In another example, the weight ratio of polymeric MDI:TDI may be from about 50:50 to about 90:10.

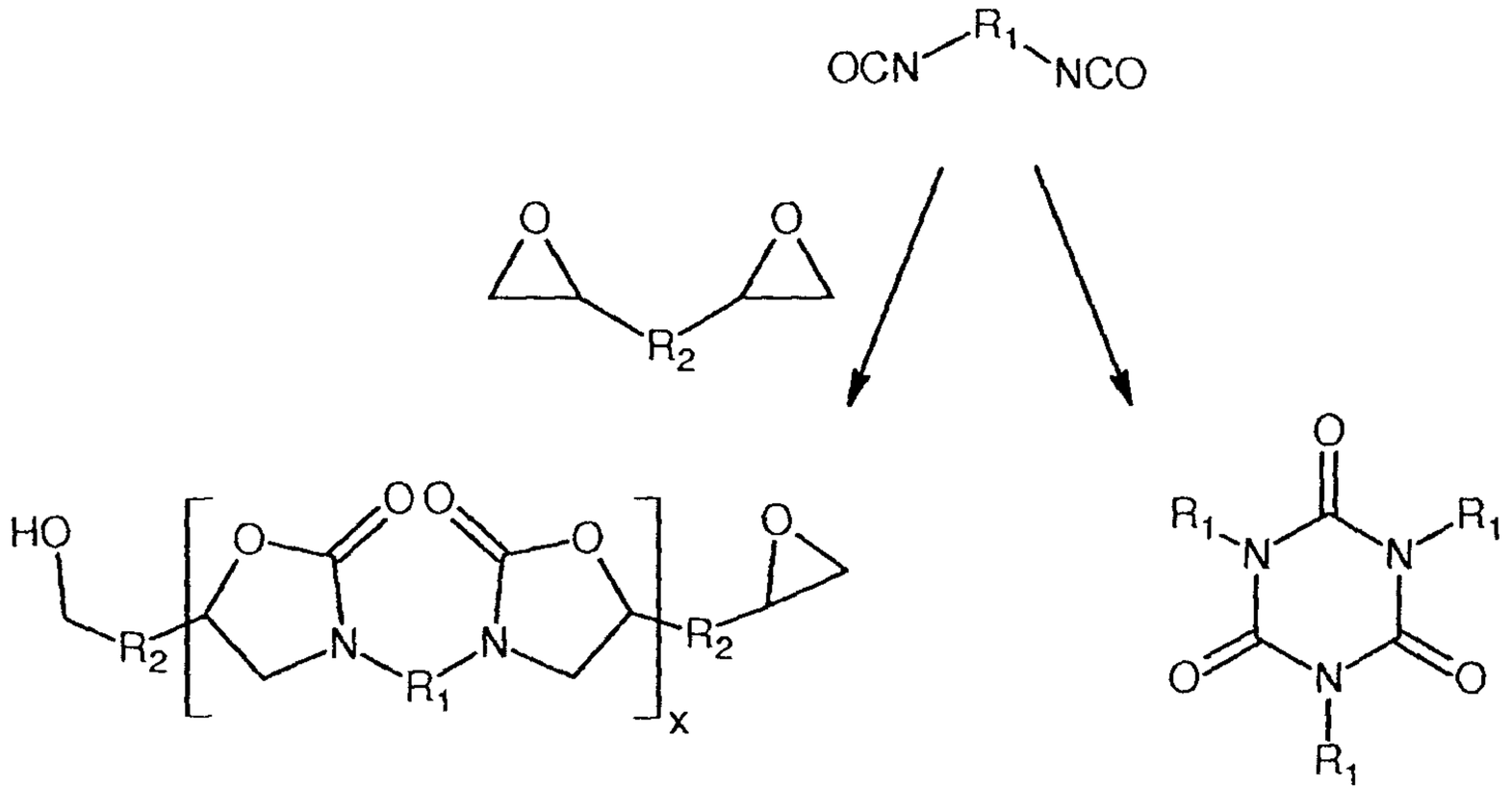
The polymeric MDI will often have an average isocyanate functionality (i.e., an average number of isocyanate groups per molecule) of not higher than about 3.5, e.g., not higher than about 3, not higher than about 2.8, or not higher than about 2.7, but usually not lower than about 2.1, e.g., not lower than about 2.2, or not lower than about 2.3.

The TDI for use in making the thermosetting polymer of the present invention may be a mixture of the 2,4- and 2,6-isomers. Commercially available TDI often contains these isomers in a ratio of about 80:20 (2,4:2,6), but any other isomer ratios such as, e.g., about 50:50, about 65:35 about 100:0 and about 0:100 are suitable as well.

In addition to the TDI and the polymeric MDI components, the isocyanate starting material for making the polymer of the present invention may comprise one or more additional isocyanate compounds. Non-limiting specific examples of such isocyanate compounds include (monomeric) MDI, methane diisocyanate, butane diisocyanate (e.g., butane-1,l-diisocyanate), ethylene-1,2-diisocyanate, trans-vinylene diisocyanate, propane-1,3-diisocyanate, 2-butene-1,4-diisocyanate, 2-methylbutane-1,4-diisocyanate, hexane-1,6-diisocyanate, octane-1,8-diisocyanate, diphenylsilane diisocyanate, benzene-1,3-bis(methyleneisocyanate), benzene-1,4-bis(methyleneisocyanate), isophorone diisocyanate, cyclohexane-1,3-bis(methyleneisocyanate), 4,4'-methylene-bis(cyclohexylisocyanate) (H_{12}MDI), 1,3- and 1,4-bis(isocyanate) methyl cyclohexane (ADI), isomers of xylenediisocyanate, bis(4-benzeneisocyanate) ether, bis(4-benzeneisocyanate) sulfide and bis(4-benzeneisocyanate) sulfone; and mixtures thereof.

It is particularly preferred if at least about 20%, e.g., at least about 50%, at least about 70%, at least about 80%, or at least about 90% by weight (e.g., about 100%) of the isocyanate starting materials for the preparation of the thermosetting polymers of the present invention are composed of polymeric MDI or a mixture of TDI and polymeric MDI.

The reaction of the epoxy groups and the isocyanate groups in the presence of a catalyst can result in two predominant types of ring structures, i.e., isocyanurate rings (through trimerization of isocyanate groups) and oxazolidinone rings (through reaction of an isocyanate group with an epoxy group). For example, the reaction of a diepoxy compound and a diisocyanate compound (carried out in the presence of a suitable catalyst at elevated temperature) can schematically be represented as follows:



In the above reaction scheme, R_1 represents a divalent residue of an aromatic diisocyanate (for example, in the case of TDI it represents CH_3-C_6H_3 and in the case of polymeric MDI it represents -C_6H_4-[CH_2-C_6H_3NCO]$_m$-CH_2-C_6H_4- with m = 1, 2, 3, etc.), and R_2 represents a divalent residue of a diepoxide (for example, in the case of the diglycidyl ether of bisphenol A, it represents CH_2-O-C_6H_4-$C(CH_3)_2$-C_6H_4-O-CH_2).

The ratio oxazolidinone rings : isocyanurate rings in the thermosetting polymer of the present invention (as can be determined by, e.g., FT-IR peak heights at 1750 and 1710 cm^{-1} for oxazolidinone and the isocyanurate, respectively) will usually be at least about 95:5 (and up to about 100:0). Preferably, the ratio will be at least about 98:2, e.g., at least about 99:1. In other words, the average value of x in the above scheme is preferably close to 0.

The ratio of oxazolidinone rings to isocyanurate rings can be influenced by varying parameters such as, e.g., reaction temperature, amount and type of catalyst(s), relative ratio of epoxy and isocyanate compounds, and rate of addition of the isocyanate component. In this regard, U.S. Patent No. 5,112,932 may, for example, be referred to. The Examples below illustrate ways in

which the desired high ratio of oxazolidinone rings to isocyanurate rings in an epoxy-terminated isocyanate modified polymer can be obtained.

The thermosetting polymer of the present invention can be prepared in a manner which is well known to those skilled in the art. In this regard, U.S. Patent No. 5,112,932 and EP 0 113 575 A1 may, for example, be referred to.

Non-limiting examples of suitable catalysts for the polymer formation, i.e., the formation of oxazolidinone rings (and isocyanurate rings) include nucleophilic amines and phosphines, ammonium and phosphonium salts. Specific examples thereof include nitrogen heterocycles such as, e.g., alkylated imidazoles (for example, 2-phenylimidazole, 2-methylimidazole, 1-methylimidazole, 2-methyl-4-ethylimidazole and 4,4'-methylene-bis(2-ethyl-5-methylimidazole); other heterocycles such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), diazabicyclooctene, hexamethylenetetramine, morpholine, piperidine; trialkylamines such as triethylamine, trimethylamine, benzyldimethylamine; phosphines such as triphenylphosphine, tritolylphosphine and triethylphosphine; quaternary ammonium and phosphonium salts such as triethylammonium chloride, tetraethylammonium chloride, tetraethylammonium acetate, tetraethyl ammonium bromide, benzyl triethyl ammonium chloride, triphenylphosphonium acetate, triphenylphosphonium iodide, ethyl triphenyl phosphonium iodide, and benzyl triphenyl phosphonium bromide. Lewis acids based on Al, Fe, Mg, or Zn such as, e.g., zinc carboxylate, organozinc chelate compounds, stannous octoate, and trialkyl aluminum compounds, and antimony containing catalysts, such as, e.g., triorganoantimony di- and tetraiodide are further non-limiting examples of catalysts that may be used for the production of the polymer of the present invention (of course, more than one catalyst may be used). The preferred catalysts are imidazole compounds. Particularly preferred catalysts are 2-phenylimidazole, 2-methylimidazole, 1-methylimidazole, 2-ethyl-4-methylimidazole, and 4,4'-methylene-bis(2-ethyl-5-methylimidazole); and mixtures thereof.

The catalyst or mixture of catalysts is generally employed in an amount of from about 0.01 % to about 2 %, e.g., from about 0.02 % to about 1 % or from about 0.02 % to about 0.1 % by weight, based on the combined weight of the epoxy and isocyanate starting materials.

The reaction is usually carried out in the absence of a solvent. The reaction temperature will usually range from about 150°C to about 180°C. Preferably, the reaction is

conducted at a temperature of from about 155°C to about 175°C. Most preferably, the reaction is conducted at a temperature of from about 160°C to about 165°C.

The thermosetting polymer of the present invention preferably has an equivalent epoxy weight (EEW) of at least about 330, e.g., at least about 350, at least about 380, or at least about 400, but usually not higher than about 1,000, e.g., not higher than about 500. As illustrated in Figure 5, there is a relationship between the EEW and the onset glass transition temperature, Tg, of the polymer, with the onset glass transition temperature increasing with increasing EEW. The EEW (and the onset glass transition temperature) can in turn be increased by increasing the digestion (incubation) time at elevated (e.g., reaction) temperature after the completion of the addition of the isocyanate components to the epoxy resin (as illustrated in Figure 4). While not wishing to be bound by any theory, it is speculated that during the digestion (incubation) period at elevated temperature hydroxy groups which are present in the polymer (derived from the hydroxy group containing epoxy resin starting material) react with epoxy groups of the polymer in the presence of a catalyst to result in branching of the polymer molecules and thus, an increased EEW (and an increased onset glass transition temperature).

The EEW is mainly dependent on the duration of the digestion period and the digestion temperature. For example, the desired EEW can be reached by controlling the digestion time. The preferred digestion temperature is in the range of from about 160°C to about 180°C, e.g., from about 165°C to about 175°C.

In order to reach a desirable EEW, the epoxy resin (with or without hydroxy groups) may also be combined with one or more di- or multifunctional nucleophilic compounds. These compounds can be added to the epoxy resin(s) before or during the polyisocyanate addition and/or after the polyisocyanate addition has been completed. Non-limiting examples of these nucleophilic compounds include amine-curing agents such as, e.g., dicyandiamide and diaminodiphenylmethane, polycarboxylic acids and anhydrides such as, e.g., phthalic anhydride, tetrahydrophthalic anhydride (THPA), methyl tetrahydrophthalic anhydride (MTHPA), hexahydrophthalic anhydride (HHPA), methyl hexahydrophthalic anhydride (MHHPA), nadic methyl anhydride (NMA), succinic anhydride and maleic anhydride, and phenolic compounds such as, e.g., tris(hydroxyphenyl)ethane or -methane, polyols such as, e.g., glycerin and tris(hydroxymethyl)methane, and the like; and mixtures thereof.

The powder coating composition of the present invention will usually comprise from about 10% to about 99% by weight of the thermosetting polymer(s) of the present invention, based on a total weight of the composition. The powder coating composition of the present invention will usually comprise at least about 10%, e.g., at least about 30%, at least about 50% or at least about 60%, but usually not more than about 99%, e.g., not more than about 95%, not more than about 90% or not more than about 85% by weight of the thermosetting polymer(s) of the present invention, based on the total weight of the composition.

Further components of the composition of the present invention may include, but are not limited to, additives selected from curing agents and curing accelerators for the crosslinking reaction between, e.g., epoxy groups and/or epoxy groups and hydroxy groups, pigments, flow control agents and fillers. Specific examples of these additives are well known to those skilled in the art.

Non-limiting examples of suitable curing agents include, but are not limited to, amine-curing agents such as dicyandiamide, diaminodiphenylmethane and diaminodiphenylsulfone, polyamides, polyaminoamides, polymeric thiols, polycarboxylic acids and anhydrides such as phthalic anhydride, tetrahydrophthalic anhydride (THPA), methyl tetrahydrophthalic anhydride (MTHPA), hexahydrophthalic anhydride (HHPA), methyl hexahydrophthalic anhydride (MHHPA), nadic methyl anhydride (NMA), polyazealic polyanhydride, succinic anhydride, maleic anhydride and styrene-maleic anhydride copolymers, as well as phenolic curing agents such as phenol novolac resins; and mixtures thereof.

Non-limiting examples of suitable curing accelerators include, but are not limited to, substituted or epoxy-modified imidazoles such as 2-methylimidazole, 2-phenyl imidazole and 2-ethyl-4-methyl imidazole, tertiary amines such as triethylamine, tripropylamine and tributylamine, phosphonium salts such as ethyltriphenylphosphonium chloride, ethyltriphenylphosphonium bromide and ethyltriphenylphosphonium acetate, and ammonium salts such as benzyltrimethylammonium chloride and benzyltrimethylammonium hydroxide; and mixtures thereof. Curing agents and accelerators are preferably used in total amounts of from about 0.5% to about 20% by weight, based on the total weight of the powder coating composition.

The powder coating composition of the present invention may be prepared by any process which blends the components of the composition substantially uniformly. For example, dry blend, semi-dry blend or melt blend procedures may be used. The blend can

then be pulverized to form the powder coating composition. Particles of the powder coating composition will preferably have a size of not more than about 300 microns.

The powder coating composition of the present invention can be applied to substrates by any desired powder coatings process such as, e.g., fluidized bed sintering (FBS), electrostatic powder coating (EPC) and electrostatic fluidized bed (EFB).

In the fluidized bed sintering (FBS) process a preheated substrate (e.g., a metal pipe) is immersed into the powder coating composition, which is kept suspended by a flow of air. The substrate to be coated is preheated to a temperature of, e.g., at least about 200°C, e.g., at least about 240°C, but usually not higher than to about 350°C, e.g., not higher than about 300°C, and contacted with the fluidized bed (e.g., immersed therein). The immersion time of the substrate depends, *inter alia*, on the desired coating thickness.

In the electrostatic powder coating (EPC) process, the powder coating composition is blown by compressed air into an applicator where it is usually charged with a voltage of about 30 to about 100 kV by a high-voltage direct current, and sprayed onto the surface of the substrate to be coated. Then it is baked in a suitable oven. The powder adheres to the cold substrate due to its charge. Alternatively, the electrostatically charged powder can be sprayed onto a heated substrate such as a pipe and allowed to cure with the residual heat of the substrate or with the help of external heat.

In the electrostatic fluidized bed (EFB) process, the above procedures are combined by mounting annular or partially annular electrodes over a fluidized bed containing the powder so as to produce an electrostatic charge of, for example, about 50 to about 100 kV. Substrates are heated at temperatures specific for the powder coating to fully cure.

Numerous substrates can be coated with the powder coating composition of the present invention. The preferred substrates are metals (e.g., iron, steel, copper), in particular metal pipes. Examples of other materials that may be coated with the powder coating composition of the present invention include ceramic and glass materials. The coating made from the powder coating composition of the present invention may find use, for example, as coating material for pipelines operating at high service temperatures (e.g., 110°C and higher).

The sintered and non sintered resins as well as the coating composition of the present invention can be also used to electrically insulate coils, transformers, and motors by coating the armatures and stators. It can also be used to coat magnet wire, bus bars, and torpid cores. Among other things, the above can be used by manufacturers of appliance

fractional horsepower motors and other applications requiring UL Electrical Insulation Systems recognition. The FBE process ensures that each powder particle comprises all of the components that are necessary to obtain a complete cure and attain the stated performance properties. Properly formulated the polymers of this invention can also be used in electrical laminate applications.

The present invention will be further illustrated by the following non-limiting Examples. In these Examples, all reactions were carried out under dry conditions with a constant dynamic purge of nitrogen. Temperatures reported below are given with an accuracy of about ± 2°C. The reaction temperature was controlled with two lamps, one of which is connected to a temperature controller (DigiSense, ID# 1603ECTC-3). Epoxy equivalent weight (EEW) values were obtained via EEW titration using a Mettler DL55 Auto-Titrator. Values of onset glass transition temperature, Tg, were determined by Differential Scanning Calorimetry (DSC).

Example 1

A glass reactor was charged with 270.84 g of a substantially oligomer (hydroxy group)-free bisphenol A diglycidyl ether (D.E.R. 332™, The Dow Chemical Company). After heating to 160-165°C, 105 mg of 2-phenylimidazole was added. Once the 2-phenylimidazole was dissolved 80.90 g of PAPI™ 94 (polymeric MDI, The Dow Chemical Company, average molecular weight 325, average isocyanate functionality 2.5) was added drop wise at 165-180°C. Thereafter the reaction mixture was incubated at 180°C for 2.5 hours. The resultant polymer had an EEW of 375 g/eq. and showed an onset Tg of 40°C.

Example 2

A glass reactor was charged with 615.5 g of bisphenol A diglycidyl ether (D.E.R. 383™ from The Dow Chemical Company) After heating to 160-165°C, 300 mg of 2-phenylimidazole (Aldrich, >98%) was added. Once the 2-phenylimidazole was dissolved 153 g of PAPI™ 94 was added drop wise at 165-180°C. Thereafter, the reaction mixture was incubated at 180°C for 0.75 hours. The resultant polymer had an EEW of 351 g/eq. and showed an onset Tg of 28.5°C.

Example 3

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A glass reactor was charged with 1193 g of bisphenol A diglycidyl ether (D.E.R. 383™ from The Dow Chemical Company) After heating to 160-165°C, 500 mg of 2-phenylimidazole (Aldrich, > 98%) was added. Once the 2-phenylimidazole was dissolved 336.5 g of PAPI 94 (polymeric MDI, The Dow Chemical Company, average molecular weight 325, average isocyanate functionality 2.5) was added drop wise at 165-180°C. Then the reaction mixture was incubated at 180°C for 0.75 hours. The resultant polymer had an EEW of 384 g/eq. and showed an onset Tg of 37.4°C.

Example 4

A glass reactor was charged with 676.0 g of bisphenol A diglycidyl ether (D.E.R. 383™, The Dow Chemical Company). After heating to 160-165°C, 320 mg of 2-phenylimidazole was added. Once the 2-phenylimidazole was dissolved 169.0 g of PAPI 27 (polymeric MDI, The Dow Chemical Company, average molecular weight 387, average functionality 2.9) was added drop wise at 165-180°C. Then the reaction mixture was incubated at 180°C for 0.75 hours. The resultant polymer had an EEW of 346 g/eq. and showed an onset Tg of 26.6°C.

Example 5

A glass reactor was charged with 1200.0 g of bisphenol A diglycidyl ether (D.E.R. 383™, The Dow Chemical Company). After heating to 160-165°C, 500 mg of 2-phenylimidazole was added. Once the 2-phenylimidazole was dissolved 319 g of PAPI 27 was added drop wise at 165-170°C. Then the reaction mixture was incubated at 170°C for 0.5 hours. The resultant polymer had an EEW of 360 g/eq. and showed an onset Tg of 31°C.

Example 6

A glass reactor was charged with 1202 g of bisphenol A diglycidyl ether (D.E.R. 383™). After heating to 160-165°C, 500 mg of 2-phenylimidazole (Aldrich, >98%) was added. Once the 2-phenylimidazole was dissolved 127.8 g of toluene diisocyanate (VORANATE™ T-80, mixture of 80:20 isomer mixture of 2,4- and 2,6-toluene diisocyanate available from The Dow Chemical Company) was added over 10 minutes, followed by a step wise addition of 191.7 g of polymeric MDI (PAPI 27) at 165-175°C. After the addition of the polymeric MDI the reaction mixture was allowed to digest for 90 minutes. The

resultant polymer had an EEW of 413 g/eq. and showed an onset Tg of 46°C. Figure 1 shows the DSC thermogram of the polymer.

Example 7a

A glass reactor was charged with 1202 g of bisphenol A diglycidyl ether (D.E.R. 383™). After heating to 160-165°C, 500 mg of 2-phenylimidazole (Aldrich, >98%) was added. Once the 2-phenylimidazole was dissolved 319 g of a 60:40 (weight %) mixture of polymeric MDI (PAPI 27) and TDI (VORANATE T-80) was added drop wise at 165-175°C. Thereafter the reaction mixture was allowed to digest for 90 minutes. The resultant polymer had an EEW of 418 g/eq. and showed an onset Tg of 45°C.

Example 7b

The same reactant ratios and reaction conditions were used as described in Example 7a, but the incubation at 180°C was conducted for 2.5 hours. Samples were analyzed for EEW, melt viscosity and Tg every 30 minutes. The obtained results are summarized in Table I. below.

Table I.

Digestion Time (min)	Onset Tg (°C)	EEW (eq/g)	Melt Viscosity (mPa.s)	
0	*40.5*	*401*	*6600*	*Extrapolated Values*
30	*41.9*	405	6628	Actual Values
60	43.4	410	6618	
90	44.5	411	6598	
120	44.9	415	6692	
150	46.3	417	6999	

Figure 4 illustrates the increase of the polymer EEW and Tg with an increase in the duration of the digestion period for a polymer which was made in a scale up of the above procedure. The relationships between the EEW and the onset Tg and the melt viscosity for this polymer are shown in Table I. and graphically represented in Figures 5 and 6.

As can be seen, there is an approximately linear increase of both the EEW and the Tg of the polymer with increasing digestion time. The melt viscosity is essentially

independent of the EEW up to an EEW of about 411 and starts to increase significantly at an EEW of about 415.

Example 7c

Example 7b (scale up version) was repeated but replacing the bisphenol A diglycidyl ether by the substantially oligomer (hydroxy group)-free bisphenol A diglycidyl ether employed in Example 1 above (D.E.R. 332™). Figure 7 shows that the polymer EEW and the Tg of the resultant polymer are substantially unaffected by an increase in the duration of the digestion period. The relationships between the EEW and the onset Tg and the melt viscosity for this polymer are shown in Table II. below and graphically represented in Figures 8 and 9.

Table II.

Digestion Time (min)	Onset Tg (°C)	EEW (eq/g)	Melt Viscosity (mPa.s)	
0	*36.8*	*374*	*2800*	*Extrapolated Values*
30	36.9	375	2838	Actual Values
60	36.8	379	2960	
90	37.0	381	2988	
120	37.6	383	3126	
150	36.8	386	3035	

Figure 10 illustrates and compares the impact of the digestion time on the onset Tg for the polymers of Examples 7b and 7c. As can be seen, an increase in the digestion time significantly increases the Tg of the polymer made from the oligomer (hydroxy group)-containing bisphenol A diglycidyl ether but has substantially no effect on the Tg of the polymer which is made from the bisphenol A diglycidyl ether which is substantially free of oligomers (hydroxy groups).

Example 8

A glass reactor was charged with 700 g of bisphenol A diglycidyl ether (D.E.R. 383™). After heating to 160-165°C, 350 mg of 2-phenylimidazole (Aldrich, >98%) was added. Once the 2-phenylimidazole was dissolved 191.4 g of a 80:20 (weight %) mixture of polymeric MDI (PAPI 27) and TDI (VORANATE T-80) was added drop wise at 165-

175°C. Thereafter the reaction mixture was allowed to digest for 90 minutes. The resultant polymer had an EEW of 415 g/eq. and showed an onset Tg of 45.3°C.

Example 9

A glass reactor was charged with 400.1 g of bisphenol A diglycidyl ether (D.E.R. 332™, The Dow Chemical Company). After heating to 160-165°C, 154 mg of 2-phenylimidazole was added. Once the 2-phenylimidazole was dissolved 106.34 g of PAPI 27 and TDI (60:40 mixture of 2,4- and 2,6-isomers) was added drop wise at 165-180°C. Thereafter the reaction mixture was incubated at 180°C for 2.5 hours. The resultant polymer had an EEW of 386 g/eq. and showed an onset Tg of 37°C. When 6.28 g of tris (hydroxyphenyl)ethane was added after 0.5 hour incubation time and the incubation was continued for two more hours, the resultant polymer had an EEW of 410 and an onset Tg of 43°C.

Example 10

A Fusion-Bonded Epoxy coating powder formulation was prepared by compounding 452.2 g of the polymer prepared in Example 2, 16.4 g of Amicure CG 1200 (dicyandiamide powder available from Air Products), 6.9 g of Epicure™ P 101 (2-methylimidazole adduct with bisphenol A epoxy resin available from Shell Chemical), 4.6 g of Curezol™ 2PHZ-PW (imidazole epoxy hardener available from Shikoku), 4.6 g of Modaflow Powder III (flow modifier, ethyl acrylate/2-ethylhexylacrylate copolymer in silica carrier manufactured by UCB Surface Specialties of St. Louis, Mo), 120.6 g of Minspar 7 (feldspar filler) and 3.0 g of Cab-O-Sil M 5 (colloidal silica available from Cabot Corp.). A steel bar heated at 242°C was immersed into the resulting coating powder, then allowed to cure for 2 min at 242°C and water quenched for 10 minutes. The resulting Fusion-Bonded Epoxy coating showed an onset Tg of 159°C and a good adhesion to the steel substrate.

Example 11

A Fusion Bonded Epoxy coating powder formulation was prepared by compounding 564.8 g of the polymer prepared in Example 3, 18.4 g of Amicure CG 1200, 8.5 g of Epicure™ P 101, 5.6 g of Curezol™ 2PHZ-PW, 5.6 g of Modaflow Powder III, 147 g of Minspar 7 and 3.8 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the

resulting coating powder then allowed to cure for 2 minutes at 242°C and water quenched for 10 minutes. The resulting Fusion-Bonded Epoxy coating showing an onset Tg of 160°C and a good adhesion to the steel substrate.

Example 12

A Fusion Bonded Epoxy powder coating formulation was prepared by compounding 468.2 g of the polymer prepared in Example 4, 17.1 g of Amicure CG 1200, 7.1 g of Epicure P 101, 4.7 g of Curezol 2PHZ-PW, 4.7 g of Modaflow Powder III, 123.4 g of Minspar 7 and 3.1 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the powder to result in a Fusion-Bonded Epoxy coating showing an onset Tg of 165°C and a good adhesion to the steel substrate.

Figure 2 shows the DSC thermogram of the cured powder coating formulation and Figure 3 shows the DSC thermogram of the corresponding FBE coating.

Example 13

A Fusion Bonded Epoxy powder coating formulation was prepared by compounding 752.3 g of the polymer prepared in Example 5, 26.61 g of Amicure CG 1200, 11.3 g of Epicure P 101, 7.49 g of Curezol 2PHZ-PW, 5 g of Modaflow Powder III, 197.3 g of Minspar 7 and 5.0 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the powder to result in a Fusion-Bonded Epoxy coating showing an onset Tg of 163°C and a good adhesion to the steel substrate.

Example 14

A Fusion Bonded Epoxy powder coating formulation was prepared by compounding 602.9 g of the polymer prepared in Example 6, 18.35 g of Amicure CG 1200, 9.22 g of Epicure P 101, 10.5 g of Curezol 2PHZ-PW, 4 g of Modaflow Powder III, 155.0 g of Minspar 7 and 4.0 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the powder to result in a Fusion-Bonded Epoxy coating showing an onset Tg of 162°C and good adhesion to the steel substrate.

Example 15

A Fusion Bonded Epoxy powder coating formulation was prepared by compounding 468.2 g of the polymer prepared in Example 7a, 17.07 g of Amicure CG 1200, 7.01 g of

Epicure P 101, 4.7 g of Curezol 2PHZ-PW, 4.7 g of Modaflow Powder III, 123.4 g of Minspar 7 and 3.1 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the powder to result in a Fusion-Bonded Epoxy coating showing an onset Tg of 160°C and good adhesion to the steel substrate.

Example 16

A Fusion Bonded Epoxy powder coating formulation was prepared by compounding 603 g of the polymer prepared in Example 8, 18.43 g of Amicure CG 1200, 9.4 g of Epicure P 101, 10.62 g of Curezol 2PHZ-PW, 4.0 g of Modaflow Powder III, 155 g of Minspar 7 and 4.0 g of Cab-O-Sil M 5. A steel bar heated at 242°C was immersed into the powder to result in a Fusion-Bonded Epoxy coating showing an onset Tg of 163 °C and good adhesion to the steel substrate.

The following Table III. summarizes Formulation Examples 10-16.

Table III.

Isocyanate Modified Epoxy Resins

Polymer from Example No.	Liquid Epoxy Resin Type	Isocyanate Type	Isocyanate Content (Weight %)	EEW (eq/g)	Polymer Onset Tg (°C)	Digestion Time (hrs)	Coating Powder Onset Tg (°C)	FBE Coating Onset Tg (°C)	Formulation From Example No.
1	D.E.R. 332	PAPI 94	23	375	40.0	2.5			
2	D.E.R. 383	PAPI 94	20	351	28.5	0.75	162	*159*	10
3	D.E.R. 383	PAPI 94	22	384	37.4	0.75	163	*160*	11
4	D.E.R. 332	PAPI 27	20	346	26.6	0.75	166	*165*	12
5	D.E.R. 383	PAPI 27	21	360	31.0	0.50	163	*163*	13
6	DER 383	PAPI 27/TDI (60/40) Step Addition	21	413	46	1.5	163	*162*	14
7a	*DER 383*	*PAPI 27/TDI (60/40) Mix Addition*	*21*	*418*	*45*	1.5	*161*	*160*	15
7b	*DER 383*	*PAPI 27/TDI (60/40) Mix Addition*	*21*	*417*	*46.3*	2.5			
7c	*DER 332*	*PAPI 27/TDI (60/40) Mix Addition*	*21*	*386*	*36.8*	2.5			
8	D.E.R. 383	PAPI 27/TDI (80/20) Mix Addition	21	415	45.3	1.5	165	*163*	16
9	DER 332	PAPI 27/TDI (60/40) Mix Addition plus THPE	21	410	43.0	2.5 and 0.5			

Although the present invention has been described in considerable detail with regard to certain versions thereof, other versions are possible, and alterations, permutations, and equivalents of the version shown will become apparent to those skilled in the art upon a reading of the specification and study of the drawings.

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CLAIMS:

1. A thermosetting epoxy-terminated oxazolidinone ring containing polymer, wherein the polymer is obtained by reacting at least one of (a1) at least one hydroxy group containing epoxy resin comprising bisphenol A diglycidyl ether and (a2) a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that forms crosslinks between epoxy groups with (b) at least one polyisocyanate compound selected from the group consisting of polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI) and a mixture of polymeric MDI and toluene diisocyanate (TDI) with the proviso that when said polyisocyanate comprises a mixture of polymeric MDI and TDI, the mixture comprises at least 20 percent by weight of said polymeric MDI; in the presence of (c) at least one catalyst which promotes a formation of oxazolidinone rings and a branching of the polymer and wherein the polymer in an uncured state has an onset glass transition temperature of at least 45°C and is capable of showing an onset glass transition temperature in a cured state of at least 160°C, wherein the weight ratio of said bisphenol A diglycidyl ether and the at least one polyisocyanate compound is from about 77:23 to about 81:19, and wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer has an epoxy equivalent weight of at least 400, and wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer is a powder coating composition suitable for producing fusion–bonded epoxy coating.

2. The polymer of claim 1, wherein at least 10% of the bisphenol A diglycidyl ether molecules are hydroxy group containing oligomers.

3. The polymer of claim 1, wherein the at least one polyisocyanate compound comprises toluene diisocyanate (TDI) and polymeric MDI; and wherein a weight ratio of polymeric MDI to TDI is from about 10:90 to about 90:10.

4. The polymer of claim 1, wherein the polymer has a ratio of oxazolidinone rings to isocyanurate rings in the polymer of from about 95:5 to about 100:0.

5. A thermosetting powder coating composition, wherein the composition comprises (a) a thermosetting polymer according to any one of claims 1 to 4; and (b) one or more curing catalysts for (a).

6. A substrate having thereon a fusion-bonded epoxy coating made from the powder coating composition of claim 5.

7. A method for providing a substrate with a fusion-bonded epoxy (FBE) coating, wherein the method comprises subjecting the substrate to a powder coating process with the powder coating composition of claim 5.

8. The method of claim 7, wherein the substrate comprises a metal substrate; and wherein the substrate comprises a pipe.

9. A coated substrate made by the method claim 7.

10. A method of making an epoxy-terminated oxazolidinone ring containing polymer which has an onset glass transition temperature in an uncured state of at least 45°C and is capable of showing an onset glass transition temperature of up to about 160°C in a cured state, wherein the method comprises (i) adding, under conditions which favor a formation of oxazolidinone rings over a formation of isocyanurate rings, at least one polyisocyanate compound selected from the group consisting of polymeric 4,4'-methylene bis(phenylisocyanate) (polymeric MDI) and a mixture of polymeric MDI and toluene diisocyanate (TDI) with the proviso that when said polyisocyanate comprises a mixture of MDI and TDI, the mixture comprises at least 20 percent by weight of said polymeric MDI to a mixture of (a1) at least one hydroxy group containing epoxy resin comprising bisphenol A diglycidyl ether and/or (a2) a combination of at least one epoxy resin and at least one di- or multifunctional nucleophilic compound that is capable of forming crosslinks between epoxy groups and (b) at least one compound which is capable of catalyzing a reaction between epoxy groups and isocyanate groups and is capable of promoting a branching of the polymer; and (ii) upon completion of the addition according to (i), keeping a resultant mixture at an elevated temperature for a time which is sufficient for an epoxy-terminated oxazolidinone ring containing polymer to branch in the presence of (b) and to afford an onset glass transition

temperature of the uncured polymer of at least 45°C, thereby producing said epoxy-terminated oxazolidinone ring containing polymer having an epoxy equivalent weight of at least 400, wherein said thermosetting epoxy-terminated oxazolidinone ring containing polymer is a powder coating composition suitable for producing fusion-bonded epoxy coating, and wherein the weight ratio of said bisphenol A diglycidyl ether and the at least one polyisocyanate compound is from about 77:23 to about 81:19.

11. The method of claim 10, wherein TDI and polymeric MDI are added separately; or wherein a mixture of TDI and polymeric MDI is added.

12. The method of claim 10, wherein the addition of the at least one polyisocyanate compound step (i) is carried out in two or more steps.

13. The method of claim 10, wherein the addition step (i) is carried out at a temperature of at least 150°C; and wherein the elevated temperature in step (ii) is at least 160°C.

14. The method of claim 10, wherein at least 10% of the bisphenol A diglycidyl ether molecules are hydroxyl group containing oligomers.

15. A polymer made by the method of claim 10.

FIG. 1

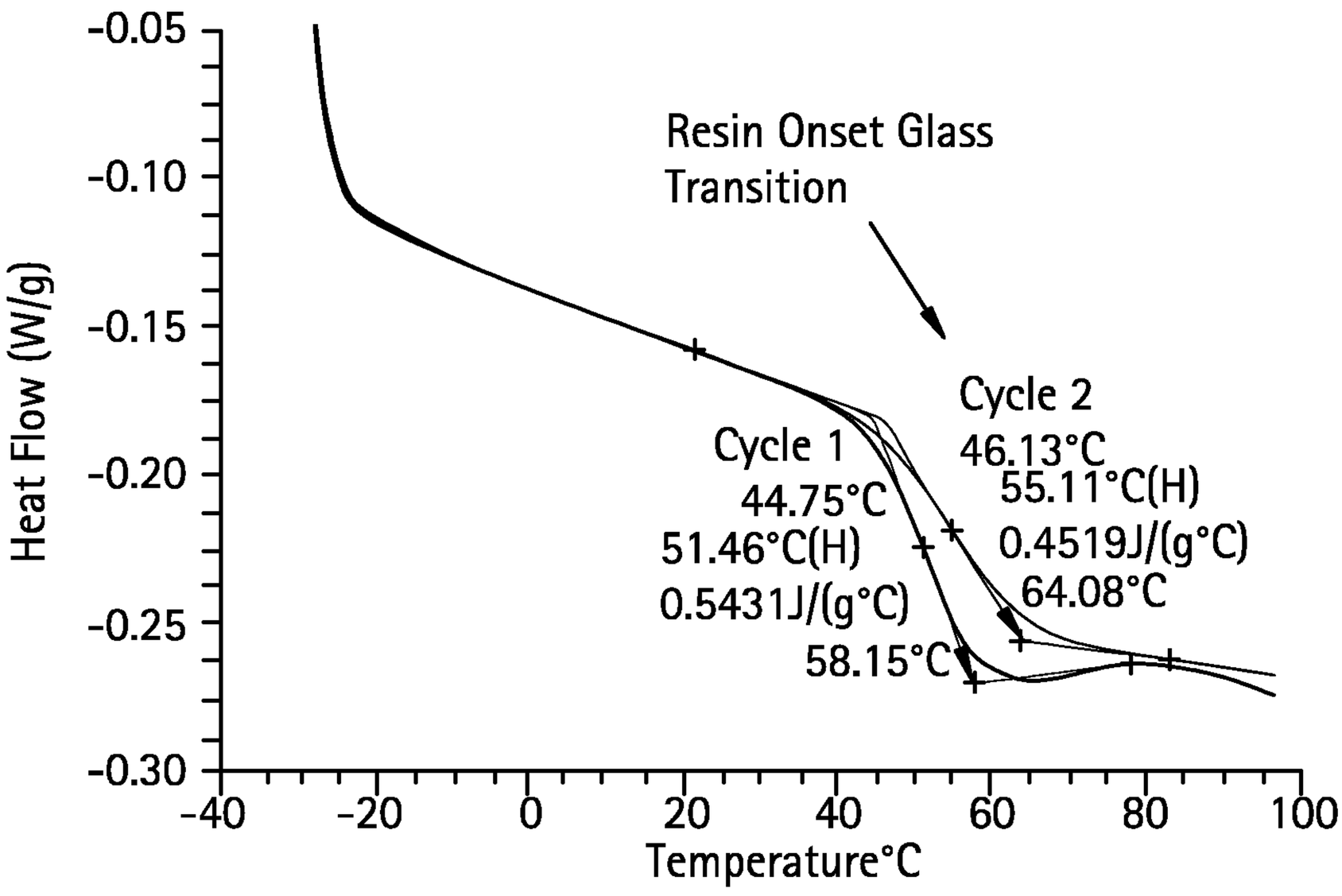

Resin Onset Glass Transition
Cycle 1
44.75°C
51.46°C(H)
0.5431J/(g°C)
Cycle 2
46.13°C
55.11°C(H)
0.4519J/(g°C)
64.08°C
58.15°C
Heat Flow (W/g)
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
-40
-20
0
20
40
60
80
100
Temperature°C

FIG. 2

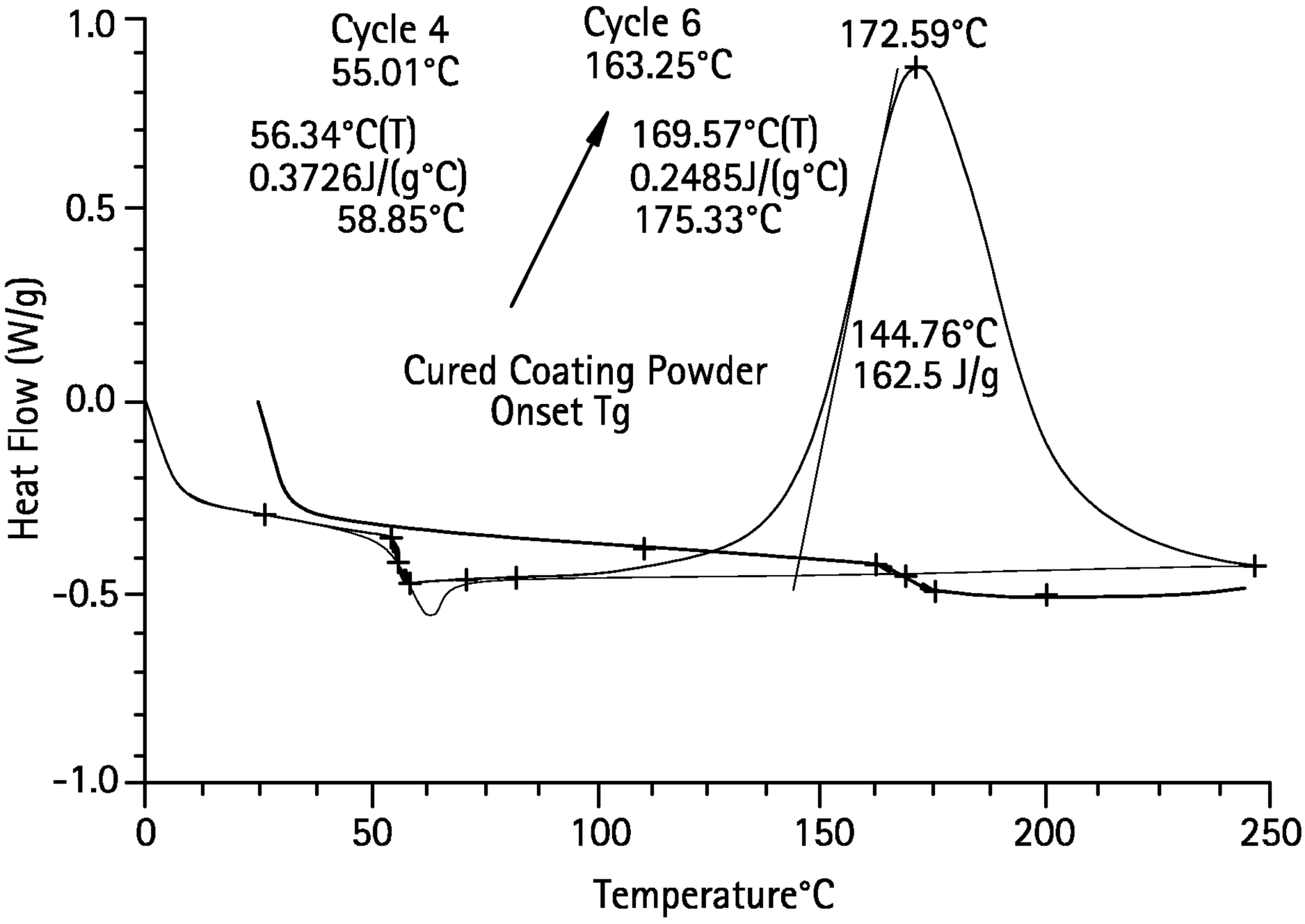

Cycle 4
55.01°C
56.34°C(T)
0.3726J/(g°C)
58.85°C
Cycle 6
163.25°C
169.57°C(T)
0.2485J/(g°C)
175.33°C
172.59°C
144.76°C
162.5 J/g
Cured Coating Powder
Onset Tg
Heat Flow (W/g)
1.0
0.5
0.0
-0.5
-1.0
0
50
100
150
200
250
Temperature°C

FIG. 3

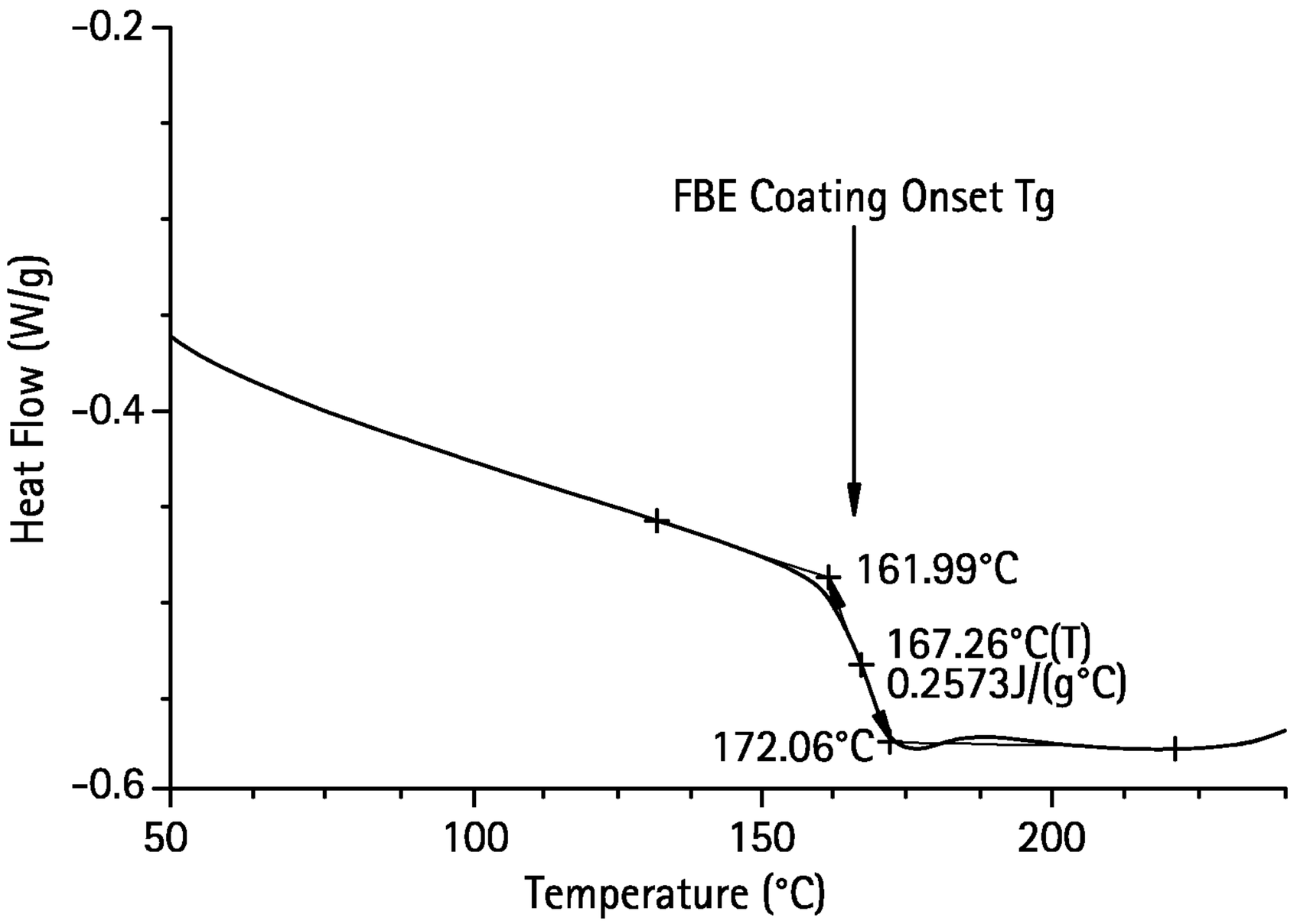

-0.2
-0.4
-0.6
Heat Flow (W/g)
50
100
150
200
Temperature (°C)
FBE Coating Onset Tg
161.99°C
167.26°C(T)
0.2573J/(g°C)
172.06°C

FIG. 4

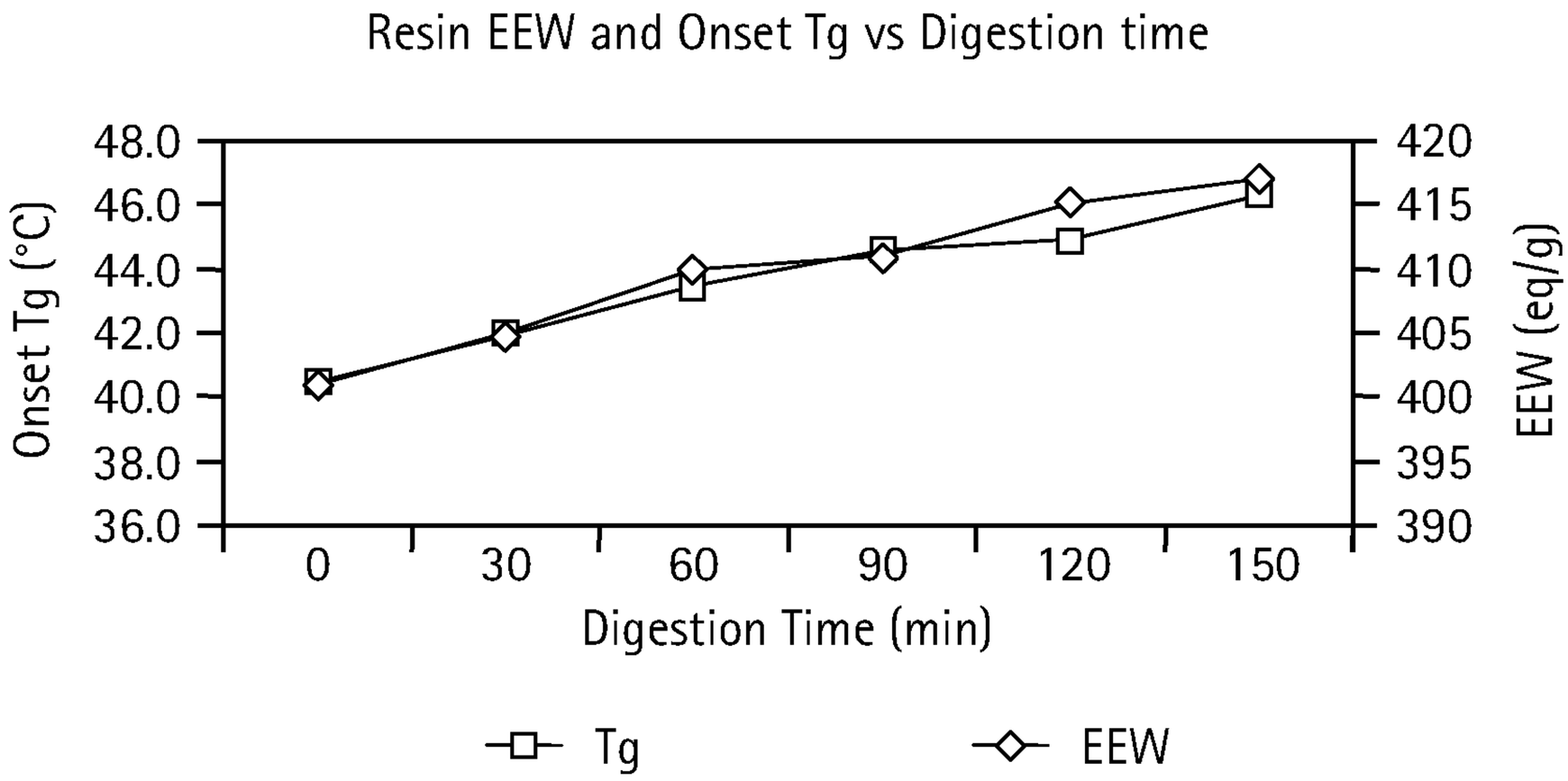

Resin EEW and Onset Tg vs Digestion time
Onset Tg (°C)
48.0
46.0
44.0
42.0
40.0
38.0
36.0
EEW (eq/g)
420
415
410
405
400
395
390
0
30
60
90
120
150
Digestion Time (min)
Tg
EEW

FIG. 5

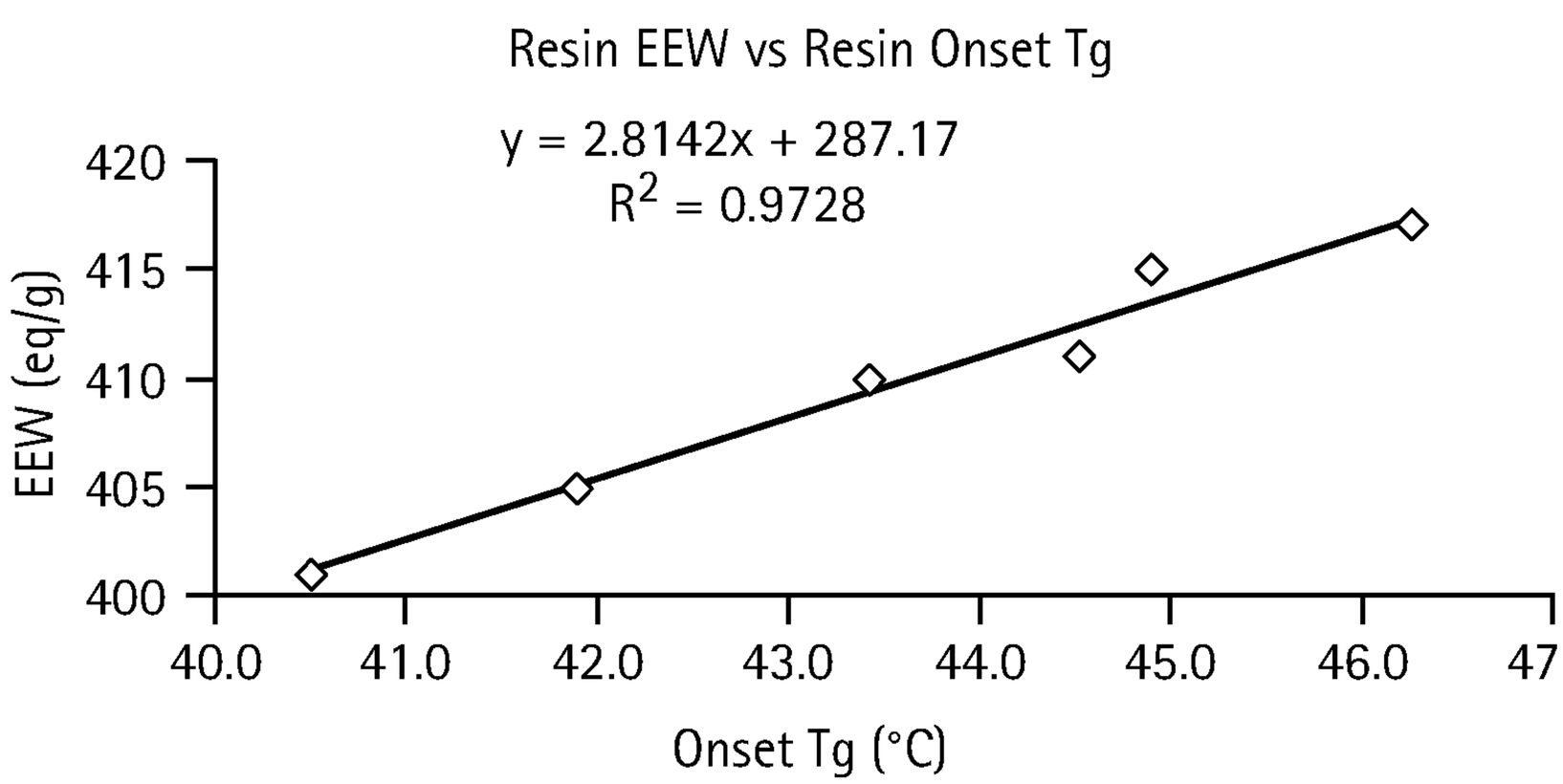

Resin EEW vs Resin Onset Tg
y = 2.8142x + 287.17
R2 = 0.9728
EEW (eq/g)
420
415
410
405
400
40.0
41.0
42.0
43.0
44.0
45.0
46.0
47.0
Onset Tg (°C)

FIG. 6

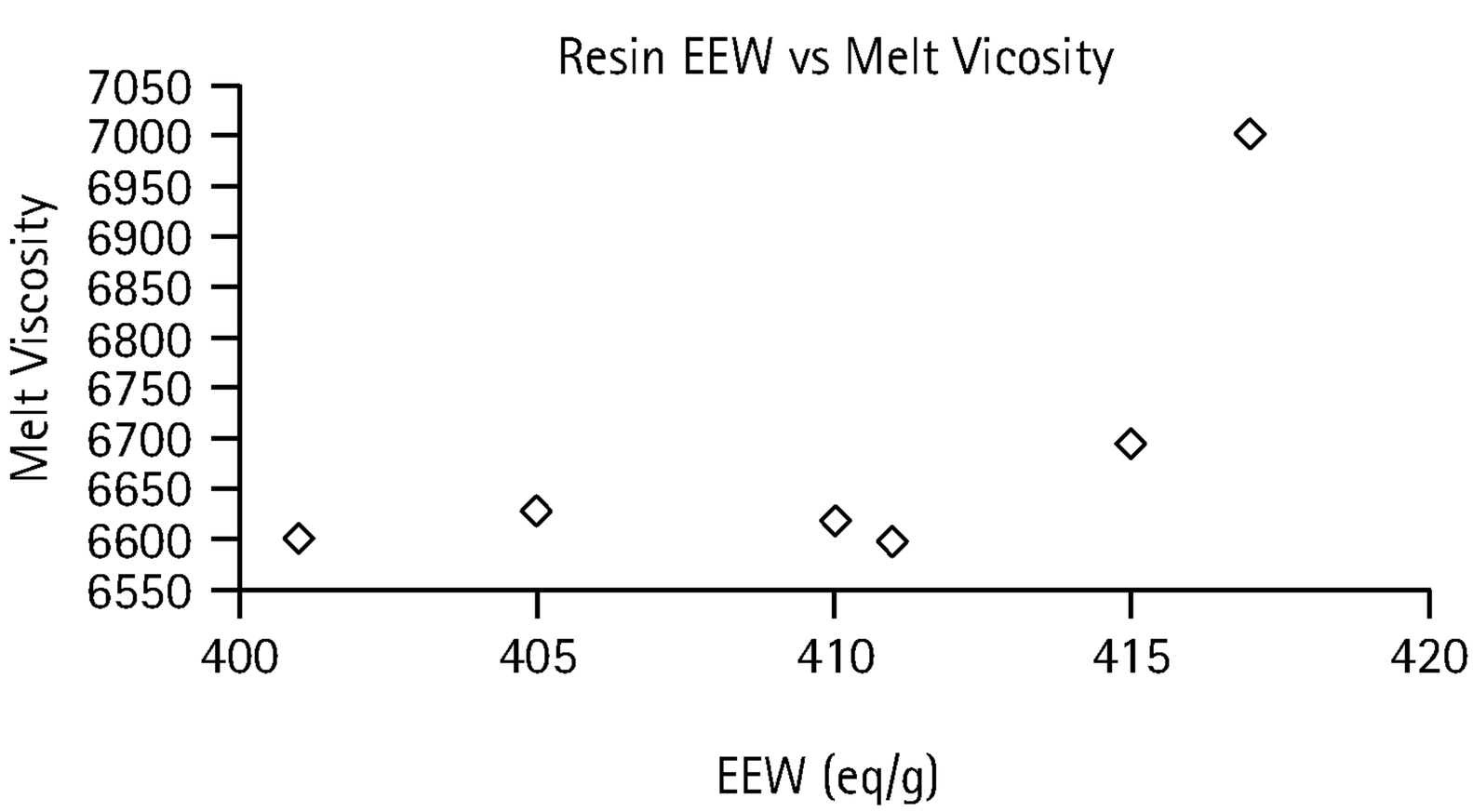

Resin EEW vs Melt Vicosity
Melt Viscosity
7050
7000
6950
6900
6850
6800
6750
6700
6650
6600
6550
400
405
410
415
420
EEW (eq/g)

FIG. 7

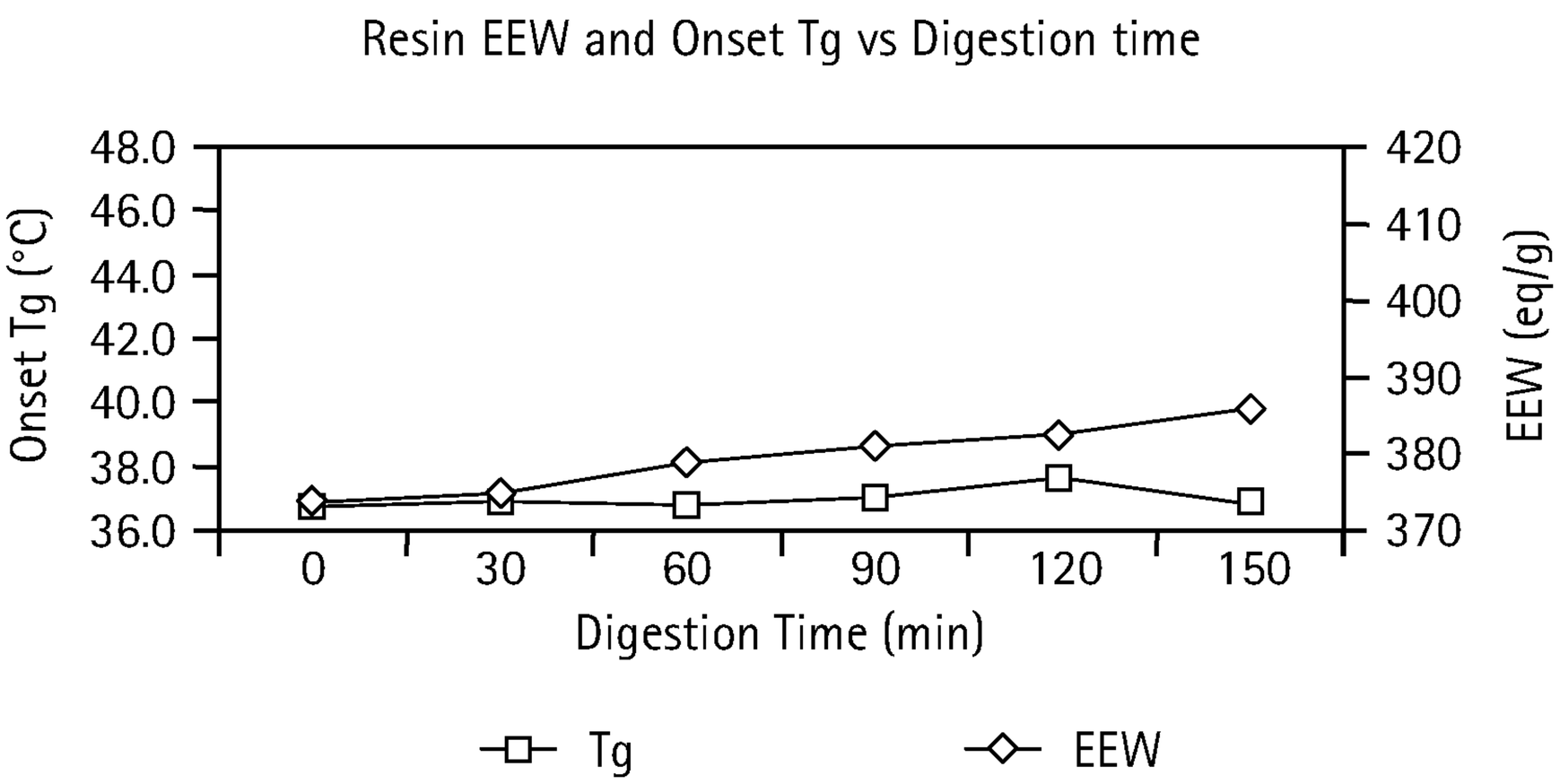

Resin EEW and Onset Tg vs Digestion time
Onset Tg (°C)
48.0
46.0
44.0
42.0
40.0
38.0
36.0
0
30
60
90
120
150
420
410
400
390
380
370
EEW (eq/g)
Digestion Time (min)
Tg
EEW

FIG. 8

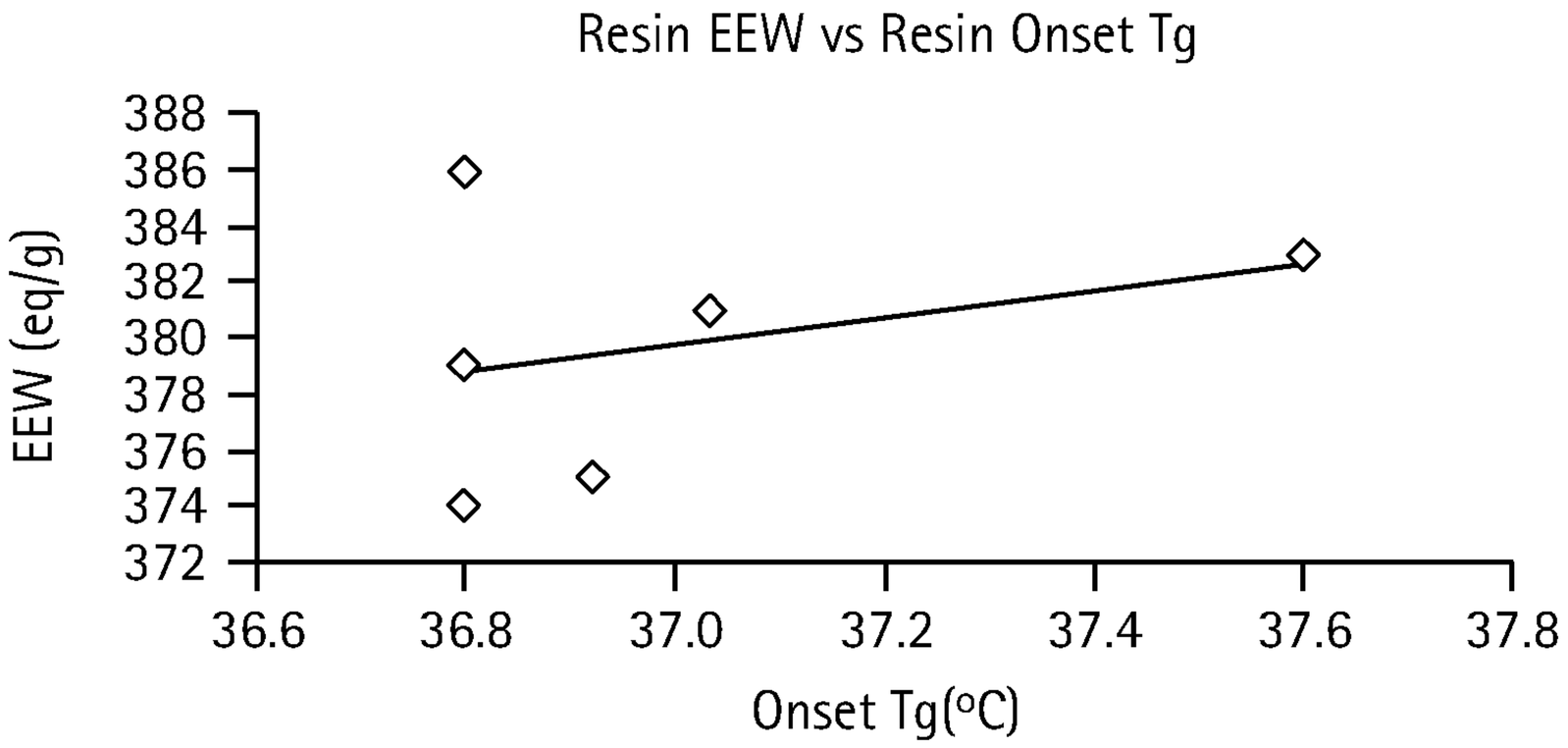

Resin EEW vs Resin Onset Tg
EEW (eq/g)
388
386
384
382
380
378
376
374
372
36.6
36.8
37.0
37.2
37.4
37.6
37.8
Onset Tg(°C)

FIG. 9

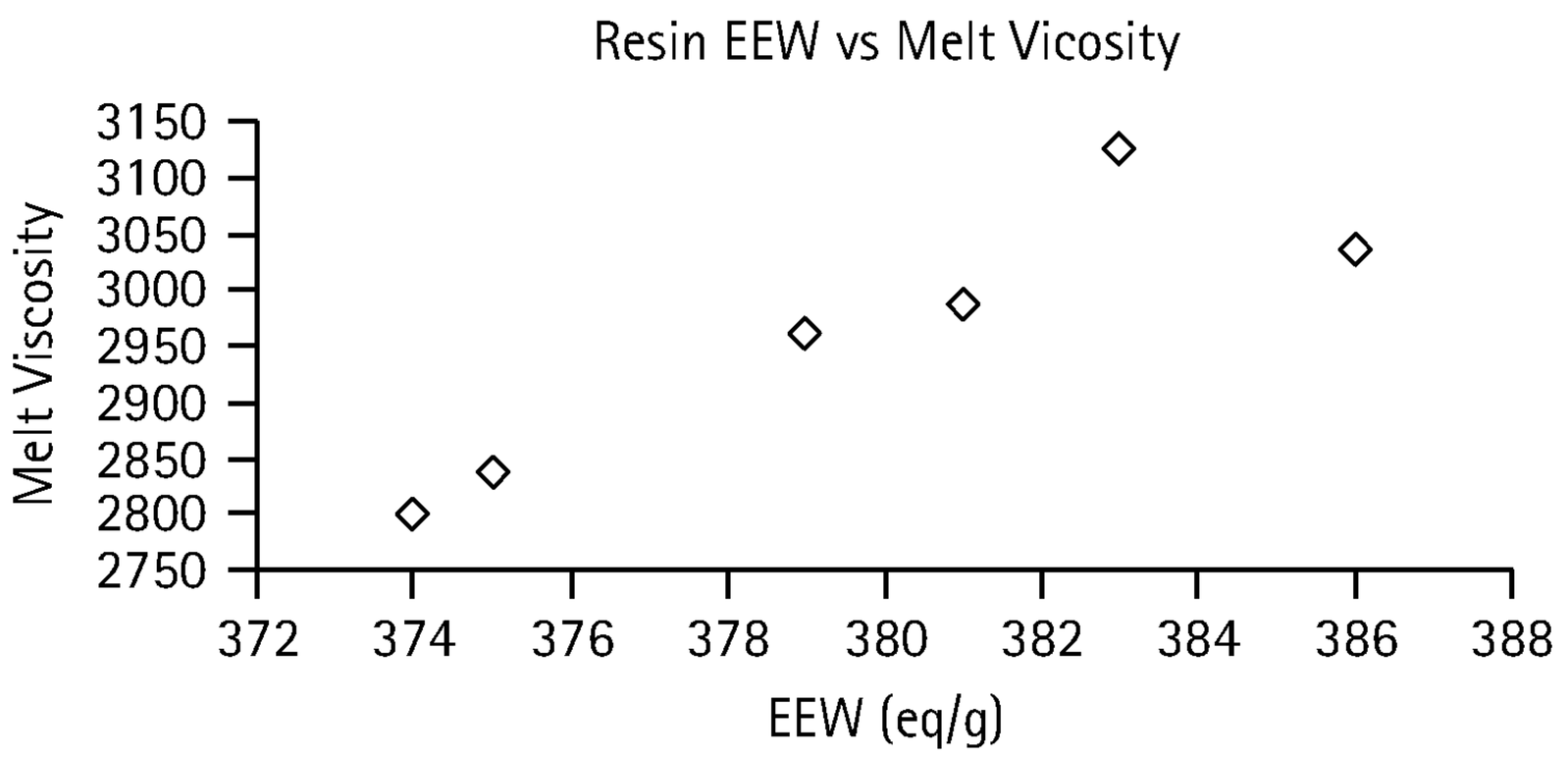
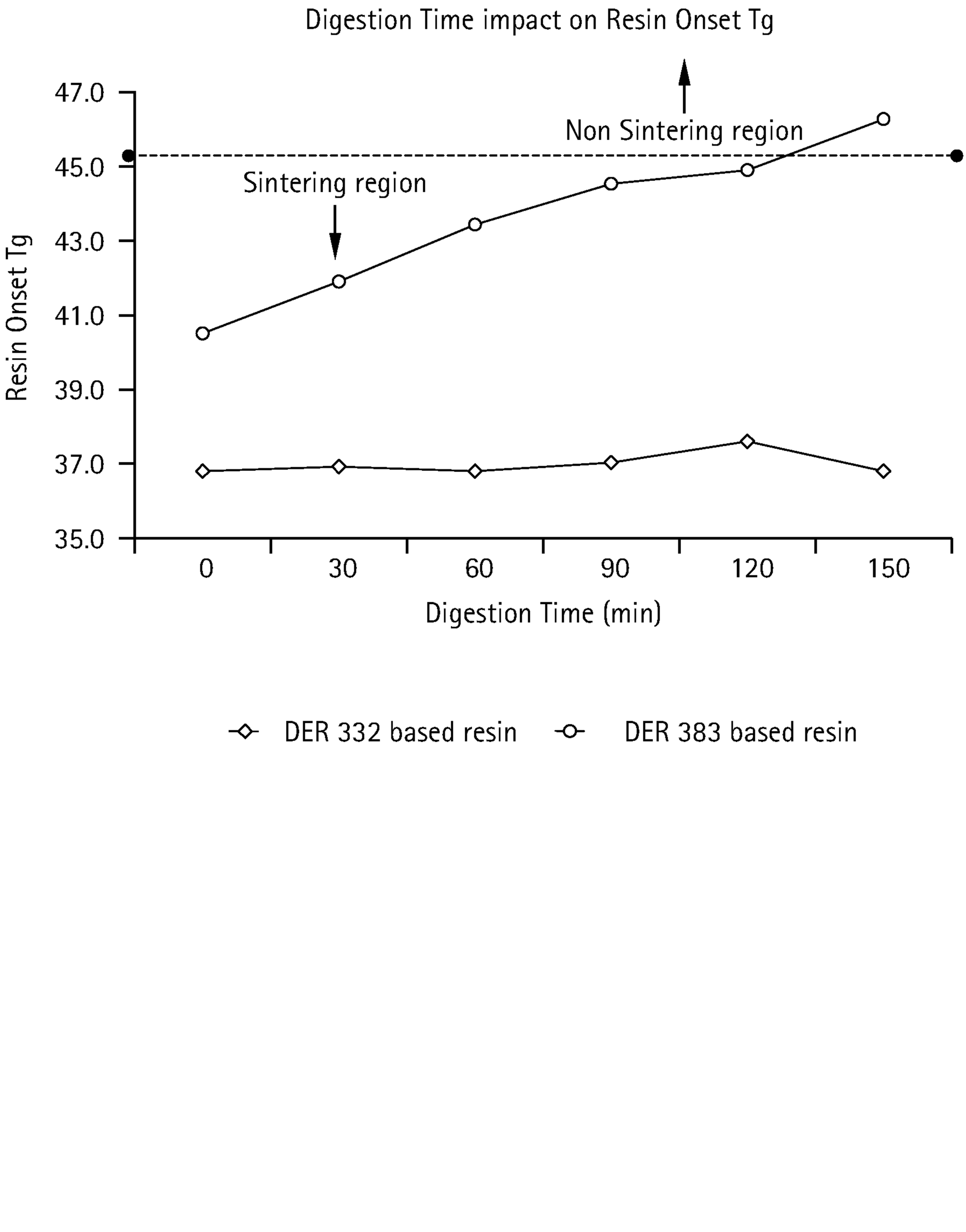

Resin EEW vs Melt Vicosity
Melt Viscosity
3150
3100
3050
3000
2950
2900
2850
2800
2750
372
374
376
378
380
382
384
386
388
EEW (eq/g)

FIG. 10


Digestion Time impact on Resin Onset Tg
Non Sintering region
Sintering region
Resin Onset Tg
47.0
45.0
43.0
41.0
39.0
37.0
35.0
0
30
60
90
120
150
Digestion Time (min)
DER 332 based resin
DER 383 based resin