Abstract:

An encapsulated curating agent, for use in a chemical composition to be cured, such as, an adhesive or encapsulant, comprises a polymeric coating forming a shell around a curing agent core. The curing agent is capable of exhibiting a morphology change and expanding upon the application of heat at a temperature below the degradation temperature of the polymeric coating material, and below the curing temperature of the encapsulant or adhesive composition in which the encapsulated curing agent is to be used. This allows the curing agent to escape from the encapsulation coating and into the composition to be cured before the cure temperature of the composition is reached.
ENCAPSULATED CURING AGENTS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to United States Provisional Patent Application No. 61/318,987 filed March 30, 2010, the contents of which is incorporated herein.

BACKGROUND OF THE INVENTION

[0002] This invention relates to curing agents encapsulated with a polymer coating that is resistant to thermal or chemical degradation. These curing agents are especially suited for use in the formulations of adhesives and encapsulants.

[0003] In a particular application, adhesives and encapsulants are used in the fabrication of semiconductor devices to attach a semiconductor to a substrate or to support and protect solder joints that electrically bond the semiconductor to a substrate, such as a circuit board. One of the requirements for a good adhesive or encapsulant is that it have a worklife sufficiently long for the fabrication operation in which it is used. Encapsulant and adhesive compositions can start to react with the curing agent and advance while being stored, resulting in an increase in viscosity. An increase in viscosity is detrimental for dispensing in many applications. Within the semiconductor industry, for example, the encapsulant or adhesive is dispensed using a syringe, and high viscosity inhibits the dispensing. Thus, a means of preventing premature cure and consequently improving worklife of adhesives and encapsulants would be an advantage.

[0004] One way to accomplish this is to block the curing agent for the adhesive or encapsulant resin until it is needed to advance cure. Methods to do this are known, for instance, by blocking the curing agent with a chemical adduct that breaks off or with a coating that degrades, when triggered by certain chemical or physical conditions. Using a chemical adduct is not always successful, because after exposure to the adhesive resin or encapsulant resin, or to a solvent in the formulation, the curing agent plus adduct may begin to break down even before deliberately triggered. Using a coating is also not always successful, because the choice of coating must be delicately balanced against the encapsulant or adhesive formulation so that it performs consistently. Release of the curing agent through a coating occurs through the degradation of the coating, triggered either thermally or chemically. A problem with this release mechanism is that the degradation does not occur instantly and for curing agents to initiate a fast cure reaction, the
full amount of curing agent is needed in a burst. External mechanical stress could initiate a
burst, but it is impractical within a chemical formulation.

SUMMARY OF THE INVENTION

[0005] This invention is an encapsulated curing agent for use in an encapsulant or adhesive
composition in which a polymeric coating forms a shell around a curing agent core.

[0006] As used within this specification and the claims, "curing agent" refers both (a) to active
neat solid or liquid catalysts, hardeners, accelerators, initiators, or any other type of curative,
commonly used to cure or harden a chosen chemical formulation, and (b) to the combination of
(i) active neat solid or liquid catalysts, hardeners, accelerators, initiators, or any other type of
curative and (ii) a polymeric matrix or porous particle in which the active curing agents are
trapped.

[0007] In all embodiments of the invention, the polymeric coating is tough enough to resist
degradation in the environment in which it is used, and the active curing agent and/or the
polymeric matrix is capable of undergoing a change in morphology and expanding in the
presence of heat. Such a change in morphology can be the result of melting or vaporization in
the case of the active curing agents, or the result of melting, vaporization, or a change from a
glassy state to a rubbery or a liquid state in the case of the polymeric matrix or porous particles.
The mechanism for the release of the active curing agent occurs through the expansion of the
curing agent and/or polymeric matrix during the morphology change, and the bursting or
degradation of the polymeric coating by the expanding curing agent and/or polymeric matrix.
The release is not dependent on any thermal transition or degradation of the polymeric coating
itself.

[0008] In a preferred embodiment, this invention is an encapsulated curing agent, for use in a
chemical composition to be cured, in which a polymeric coating forms a shell around the curing
agent core, the encapsulated curing agent comprising:

(A) a curing agent capable of undergoing a morphology change and expanding upon
the application of heat at a temperature below the disintegration temperature of
the polymeric coating material, and below the curing temperature of the chemical
composition to be cured; and
(B) a polymeric coating encasing the curing agent and capable of resisting chemical degradation in the chemical composition to be cured, or thermal degradation at the temperature at which the curing agent undergoes a morphology change.

DETAILED DESCRIPTION OF THE INVENTION

[0009] In the case in which the active neat curing agent is in the form of solid particles, the solid particles will be capable of undergoing a morphology change at a temperature below the degradation temperature of the polymeric coating material, and below the curing temperature of the encapsulant or adhesive composition in which the encapsulated curing agent is to be used. In this solid neat form, the curing agent particles can be coated directly with the desired coating material.

[0010] Examples of solid active curing agents that are suitable for encapsulation include 2-methyl imidazole (Imicure AMI-2); 2-phenyl imidazole (Curezol 2PZ); 2-phenyl-4-methyl imidazole (Curezol 2P4MZ); 2-heptadecyl imidazole (Curezol C17Z); 2-phenyl-4,5-dihydroxymethyl imidazole (Curezol 2PHZ-S); 2,4-diamino-6(2'-methylimidazolyl-(r)) ethyls-triazine (Curezol 2MZ Azine); 2,4-diammo-6[2'-methyliminu^azolyl-(10]ethyl-s-triazine, isocyanuric (Curezol 2MA-OK); triphenylphosphine; dicyandiamide; 3-phenyl-1,1-dimethyl urea; 5-amino-1-naphthol, 8-hydroxyquinoline, and the like.

[0010] In one embodiment, the neat particle size of the active solid curing agent before coating ranges from 0.1 μm to 500 μm. In another embodiment, the neat particle size of the active solid curing agent before coating ranges from 2 μm to 200 μm.

[0011] Active solid curing agents can be ground to the desired particle size. If not relatively spherical in shape and devoid of sharp edges they can be tumbled in a mechanical tumbler after being ground until they are more spherical and smoother. This makes them easier to coat and eliminates chipping of the coating off the core curing agent.

[0012] Emulsification can also be used to provide active solid curing agents desired in small sizes. In a typical procedure, the curing agent particles are added to water, or an organic solvent as appropriate, and heated under agitation to a temperature sufficient to dissolve the particles. A surfactant is added under vigorous stirring to reduce the average size of the particles. The higher the level of surfactant and the more vigorous the stirring, the smaller the particle size will be. The exact ratio of surfactant and shear will vary per the curing agent, but can be determined by one skilled in the art without undue experimentation. The solution is then rapidly cooled, for
example, by pouring it into a sufficient quantity of 0°C water. The curing agent will solidify into spherical particles. The slurry can then be filtered and air dried, and the particles collected for coating.

[0013] In another embodiment, the active curing agent can be in the form of a liquid that is entrapped in a polymeric matrix or a porous particle. Examples of active liquid curing agents include 2-ethyl-4-methyl imidazole, 1-benzyl-2-methyl-imidazole, Cu(II) naphthenate, Co(II) 2-ethyl-hexanoate, diazabicyclo-undecene, N, N-dimethylaniline, N,N-dimethyltoluidine, and the like. The liquid curing agent may be used neat, or it can be dissolved in a solvent. It is also possible to dissolve solid curing agents as described above in a suitable solvent to use them in liquid form.

[0014] In the case in which the active curing agent is in the form of a neat liquid or a solution, and a porous particle is used to entrap, suitable porous particles include, for example, silica, alumina, zeolite, molecular sieves, glass, carbon black, boron nitride, calcium carbonate, clay, and polymers (including polystyrene, polyacrylate, polyvinyl chloride, polyvinyl alcohol, polyvinylpyrrolidone, and polyurethane).

[0015] The neat liquid or solution should be of sufficiently low viscosity for saturating the porous particle. The liquid active curing agent or solution of active curing agent is added to the porous particles until the particles are saturated. The solvent, if one is used, is then evaporated off, by air drying, spray drying, or freeze drying, or any other effective method for removing the solvent without triggering a phase change of the curing agent.

[0016] The concentration of the active curing agent in the solvent can be manipulated to affect the level of loading into the porous particle, the more concentrated the curing agent in the solvent, the higher the level of loading. To further increase the loading level, additional rounds of saturation of the porous particle and evaporation of solvent can be conducted before the coating operation is performed.

[0017] For typical applications, for example, within the semiconductor industry, the porous particles are chosen to be within a size range of 1μm to 200μm; the size, however, can be any effective size and is determined by the end use application.

[0018] In the case in which the active curing agent is in the form of a neat liquid or a solution, and a polymeric matrix is used, suitable polymeric materials for trapping the active liquid curing
agents include, for example, polymethyl methacrylate, polybutyl acrylate, polystyrene, polycarbonate, cellulose acetate butyrate, polybutyral, polycaprolactone, and polylactic acid.

[0019] Entrapment of the liquid curing agents can be accomplished through a number of processes, including solvent evaporation, spray drying, and freeze drying.

[0020] In the solvent evaporation method, the polymer and active curing agent are dissolved together in an organic solvent capable of dissolving both. The solution is then emulsified in water in the presence of suitable surfactants. The organic solvent is evaporated off to solidify the particles, and the solid particles of polymeric encapsulated curing agent are collected after filtering, washing, and drying.

[0021] In the spray drying method, the active curing agent is mixed with the polymer in water or in a suitable solvent. The solution is ejected through a spray dryer and rapidly dried, and the dried particles of polymeric encapsulated curing agent are collected.

[0022] In the freeze drying method, the active curing agent is mixed with the polymer in water or solvent and the mixture is frozen. The water or solvent is removed at reduced pressure leaving behind dried material of polymeric encapsulated curing agent, which can be collected and used as is, or further treated by grinding and/or tumbling to a desired particle size.

[0023] In addition to the above methods, any other method to evaporate the solvent can be used, provided it does not trigger a phase change of the active curing agent or the polymeric matrix.

[0024] In all embodiments, either the active curing agent, or the polymeric matrix, or both, will be capable of undergoing a morphology change at a temperature below the degradation temperature of the polymeric coating material, and below the curing temperature of the encapsulant or adhesive composition in which the encapsulated curing agent is to be used.

[0025] The polymeric coating material can be any polymeric material capable of forming a coating that is resistant to degradation in the presence of the solvent and resins used to formulate the encapsulant or adhesive composition to be cured, and is also resistant to thermal degradation at the temperature at which the curing agent undergoes a change in morphology and expands. To allow fast release of the curing agent to enable rapid cure, the polymeric coating material will have suitable mechanical strength at the temperature at which the curing agent undergoes a change in morphology so that it can be burst by the volume expansion of the curing agent.

[0026] Polymeric coating materials suitable for coating the neat particulate curing agents or the curing agents trapped within a polymeric matrix or a porous particle include cross-linked or high
melting point polymers. Examples include poly(p-xylylene) (parylene); crosslinked epoxies, e.g. bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol A epoxy novolac, bisphenol F epoxy novolac, 3,4 epoxy cyclohexyl methyl, 3,4 epoxy cyclohexyl carboxylate; crosslinked acrylates, e.g. hexanediol di(meth)acrylate, polyethylene glycol di(meth)acrylate, ethoxylated bisphenol A di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, and tricyclodecane dimethanol diacrylate.

[0027] In one embodiment, the curing agents, as neat active agents, or entrapped within a polymeric matrix or porous particle, are coated by vapor deposition. Processes for vapor deposition are known in the art, and in general occur by condensing and polymerizing the monomer for forming the coating directly onto the particle to be coated. (In the case of parylene, the parylene monomer is not stable and the parylene dimer is used as the starting material. It is pyrolytically cleaved to form a reactive monomer.) The monomer is heated to vaporization and the monomer vapor is transferred to a deposition chamber in which the particles to be coated are being tumbled, such as by air or mechanically. The process is carried out in a closed system under constant negative pressure.

[0028] In another embodiment, the curing agents are coated by an interfacial polymerization process. The particles to be coated (either solids or liquid droplets) are suspended in an incompatible liquid medium (a solvent that does not dissolve the curing agent) in the presence of a suitable surfactant. The choice of surfactant is within the expertise of one skilled in the art. A monomer, insoluble in the liquid medium, is slowly added to the slurry. The monomer surface tension in the presence of the surfactant causes the monomer to be driven to the interface between the curing agent phase and the liquid media phase. Polymerization of the monomer is initiated by heat or UV to form a solid coating on the curing agent.

[0029] In a further embodiment, the interfacial polymerization method can also be used for active curing agents trapped in porous carrier particles. The active curing agent is treated so that it is in a relatively well defined spherical shape and then loaded into a porous particle as described herein. The loaded porous particle is then suspended in a liquid medium in the presence of surfactant, and a coating resin is introduced into the medium. The coating resin is driven to the particle surface and fully surrounds the particles. Heat is applied to polymerize the resin and form a thin layer of coating on the particles. The particles are filtered, washed, and dried to form the encapsulated curing agent.
In yet another embodiment, the curing agent, either as solid active curing agent or active curing agent trapped in porous particles or polymeric matrices, is coated using a fluidized bed coating operation.

In all embodiments, the coating weight is generally within the range of 0.2% to 50% of the curing agent weight.

These encapsulated curing agents are used to cure resins used in adhesive and encapsulant compositions. Such resins are well known in the art, and include, for example, epoxies and oxetanes, compounds containing carbon to carbon double bonds, isocyanates, oxazolines, benoxazines, and cyanate esters. Curing agents for these compounds are also well known in the art. However, in the instant invention, the choice of curing agent is made so that the temperature at which it exhibits a morphology change, typically its vaporization or melting point, will be below the degradation temperature of the polymeric coating material, and below the curing temperature of the encapsulant or adhesive composition in which the encapsulated curing agent is to be used. This allows the curing agent to escape from the encapsulation coating and into the composition to be cured before the cure temperature of the composition is reached.

EXAMPLES

In the following examples, worklife was measured as change in viscosity, the higher the viscosity increase, the shorter the worklife. All viscosity measurements were done at 25°C using an ARES rheometer with 25 mm parallel plates, the gap between the plates set at 1.0mm, and at a steady shear rate of 1/second.

EXAMPLE 1. WORKLIFE OF COATED AND UNCOATED CATALYST IN EPOXY-PHENOLIC RESIN

The uncoated catalyst was 2-heptadecylimidazole (purchased as Curezol C-17Z from Air Products). The coating for the catalyst was parylene C, (polychloro-para-xylylene) coated at 16% by weight of the coated catalyst. Parylene C has the following structure:

The melting behavior of the uncoated catalyst and the coated catalyst were compared using differential scanning Calorimetry (DSC, TA Q100). The samples were scanned from 30°C
to 250°C at a scanning rate of 10°C/min. The results are disclosed in TABLE 1-A and show that
the melting behavior of the parylene C encapsulated C-17Z is almost identical to the neat C-17Z.

<table>
<thead>
<tr>
<th>TABLE 1-A</th>
<th>MELTING BEHAVIOR OF COATED AND UNCOATED CATALYST</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UNCOATED CATALYST</td>
</tr>
<tr>
<td>Onset melting temperature (°C)</td>
<td>87.35</td>
</tr>
<tr>
<td>Peak melting temperature (°C)</td>
<td>90.46</td>
</tr>
<tr>
<td>Melting delta H (J/g)</td>
<td>215.2</td>
</tr>
<tr>
<td>Melting delta H (J/g of C-17Z)</td>
<td>215.2</td>
</tr>
</tbody>
</table>

[0037] The resin formulation to be cured by the catalyst had the following composition:
- bisphenol A epoxy (EPON 826 from Hexion) 10 parts by weight
- diallylbisphenol A (from Bimax) 9 parts by weight

[0038] The coated and uncoated catalysts were added to the resin formulation. The uncoated
catalyst was added at 0.83 parts by weight; the coated catalyst was added at 1.00 parts by weight
(to conform amount of catalyst at concentration of 4.2% of total formulation). Viscosity
measurements were taken after 24 hours, 48 hours, and 72 hours, at 25°C, and the percentage
increase in viscosity reported in TABLE 1-B. The results show that the formulation with the
coated catalyst had a longer worklife than the formulation with the uncoated catalyst.

<table>
<thead>
<tr>
<th>TABLE 1-B</th>
<th>RESIN FORMULATION WITH UNCOATED CATALYST</th>
<th>RESIN FORMULATION WITH COATED CATALYST</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity and percent increase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial viscosity</td>
<td>28.7 Pa.s</td>
<td>24.7 Pa.s</td>
</tr>
<tr>
<td>Viscosity after 24hrs</td>
<td>66.7 Pa.s</td>
<td>31.7 Pa.s</td>
</tr>
<tr>
<td>Viscosity after 48hrs</td>
<td>95.2 Pa.s</td>
<td>35.1 Pa.s</td>
</tr>
<tr>
<td>Viscosity after 72hrs</td>
<td>536.8 Pa.s</td>
<td>70.3 Pa.s</td>
</tr>
<tr>
<td>% Viscosity increase at 24hr</td>
<td>133%</td>
<td>28%</td>
</tr>
<tr>
<td>% Viscosity increase at 48hr</td>
<td>236%</td>
<td>42%</td>
</tr>
<tr>
<td>% Viscosity increase at 72hr</td>
<td>1772%</td>
<td>185%</td>
</tr>
</tbody>
</table>

[0039] EXAMPLE 2. WORKLIFE AND CURING SPEED OF EPOXY-PHENOL FORMULATION WITH
TRIPHENYLPHOSPHINE

[0040] The uncoated catalyst was triphenylphosphine (purchased from Sigma-Aldrich). The
coating for the catalyst was parylene N (polypara-xylylene) coated at 16% by weight of the
coated catalyst.

[0041] Parylene N has the structure:
The resin formulation to be cured by the catalyst had the following composition:

- Bisphenol A epoxy (EPON 826 from Hexion) 1.21 parts by weight
- Diallyl bisphenol A (from Bimax) 1.03 parts by weight

The coated and uncoated catalysts were added to the resin formulation. The uncoated catalyst was added at 0.27 parts by weight; the coated catalyst was added at 0.32 parts by weight (to conform amount of catalyst at 10.6% of total formulation). Viscosity measurements were taken after 24 hours and 48 hours at 25°C, and the percentage increase in viscosity reported in TABLE 2. The results show that the resin formulation containing the coated catalyst had a slower increase in viscosity and, consequently, a longer worklife than the resin formulation containing the uncoated catalyst.

DSC measurements for the resin formulations were run and the results also reported in TABLE 2. The formulations were scanned in DSC from 30°C to 250°C at 10°C/min. The results are reported in TABLE 2 and show that the curing speed was not affected significantly by the parylene coating. The DSC peak curing temperatures for both formulations were well below 120°C, indicating that both formulations can be cured at 120°C within 20 minutes.

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Viscosity and Percent Viscosity Increase and DSC</th>
<th>Resin Formulation with Uncoated Catalyst</th>
<th>Resin Formulation with Coated Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity immediately after mixing</td>
<td>1315.0 Pa.s</td>
<td>51.5 Pa.s</td>
<td></td>
</tr>
<tr>
<td>5hr viscosity</td>
<td>solid</td>
<td>52.5 Pa.s</td>
<td></td>
</tr>
<tr>
<td>24hr viscosity</td>
<td>solid</td>
<td>67.6 Pa.s</td>
<td></td>
</tr>
<tr>
<td>48hr viscosity</td>
<td>solid</td>
<td>121.1 Pa.s</td>
<td></td>
</tr>
<tr>
<td>% Viscosity increase after 5 hours</td>
<td>solids</td>
<td>2%</td>
<td></td>
</tr>
<tr>
<td>% Viscosity increase after 24 hours</td>
<td>solids</td>
<td>31%</td>
<td></td>
</tr>
<tr>
<td>% Viscosity increase after 48 hours</td>
<td>solids</td>
<td>135%</td>
<td></td>
</tr>
<tr>
<td>DSC onset curing temperature (°C)</td>
<td>70.51</td>
<td>81.22</td>
<td></td>
</tr>
<tr>
<td>DSC peak curing temperature (°C)</td>
<td>103.47</td>
<td>110.87</td>
<td></td>
</tr>
<tr>
<td>DSC curing delta H (J/g)</td>
<td>278.3</td>
<td>293.9</td>
<td></td>
</tr>
</tbody>
</table>

EXAMPLE 3. CATALYST TRAPPED IN POROUS PARTICLE AND ENCAPSULATED WITH CROSSTLINKED EPOXY
Solid 2-phenyl-4-methyl imidazole (20g) (Curezol 2P4MZ imidazole from Air Products) was dissolved in methanol (Sigma-aldrich) to provide a 40% solution. The solution was added into 10g porous silica particles (Sunsphere H52). The solvent was evaporated off, and 5g of a crosslinkable epoxy resin (Epon 826 from Hexion, a low viscosity bisphenol A epoxy resin) was added to the particles until absorbed into the rest of the pore spaces in the silica spheres. A speedmixer was used to ensure uniformity. The coated catalyst was then cured at 120°C for 30 minutes to create the encapsulant shell.

The catalyst was added neat in an amount of 6% by weight to bisphenol A epoxy (Epon 826 from Hexion, a low viscosity bisphenol A epoxy resin). The coated catalyst was added in an amount of 15% by weight to the same bisphenol A epoxy. The viscosity increase was monitored over four days. The formulation with the uncoated catalyst showed an increase in viscosity in less than two days. The coated catalyst did not show an increase in viscosity until after four days, indicating that liquid catalysts can be trapped in a porous particle and be prevented from advancing cure for longer than the unprotected catalyst. The results are reported in the TABLE 3.

<table>
<thead>
<tr>
<th>RESIN FORMULATION</th>
<th>Initial viscosity (Pa*s)</th>
<th>48 hr viscosity (Pa*s)</th>
<th>% Viscosity increase after 48h</th>
</tr>
</thead>
<tbody>
<tr>
<td>with neat 2P4MZ</td>
<td>10.5</td>
<td>18.6</td>
<td>77.1%</td>
</tr>
<tr>
<td>with encapsulated 2P4MZ</td>
<td>11.7</td>
<td>12.1</td>
<td>3.4%</td>
</tr>
</tbody>
</table>

Example 4

The releasing mechanism of an imidazole coated with parylene C was studied under hot-stage microscope. A sample of parylene C coated encapsulated 2-heptadecylimidazole was heated from 30°C to 125°C at 5°C per minute and held at 125°C for 15 minutes. The particles appeared to begin melting at approximately 77°C and completed melting by approximately 92°C. As soon as the core material passed its melting point, 85°C, the coating collapsed and melted imidazole flowed out. A web-like film of material, possibly the parylene C, remained even when the sample was held at 125°C for 15 minutes. The releasing mechanism is due to the pressure generated by the melted imidazole and resulted in imidazole bursting out of parylene C shell.
WHAT IS CLAIMED:

1. An encapsulated curing agent, for use in a chemical composition to be cured, in which a polymeric coating forms a shell around the curing agent core, the encapsulated curing agent comprising:

   (A) a curing agent core capable of undergoing a morphology change and expanding upon the application of heat at a temperature below the degradation temperature of the polymeric coating shell, and below the curing temperature of the chemical composition to be cured; and

   (B) a polymeric coating shell encasing the curing agent core and capable of resisting chemical degradation in the composition to be cured or thermal degradation at the temperature at which the curing agent undergoes a morphology change.