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单组分银粉导电胶的制备与研究

Preparation and Study on One-part Ag Electrical Conductive Adhesives

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Preparation and Study on One-part Ag Electrical Conductive Adhesives

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中文摘要

随着微电子工业的不断发展及无铅化的环保要求，导电胶受到了越来越多的重视，显示出广阔的市场前景。单组分导电胶是导电胶中的一个重要品种，它是由基体树脂、导电填料、固化剂和各种助剂混合搅拌均匀所得到的，与双组分导电胶相比，施工方便，更具商业价值。但单组分导电胶存在室温储存期短、固化强度低等不足，针对这些问题，本文分别采用封闭型聚氨酯和潜伏型环氧树脂作为基体树脂，银粉作为导电填料，并添加各种助剂，制备了一系列的单组分导电胶，并对其性能进行了表征。具体工作内容如下：

1. 以 2,4-甲苯二异氰酸酯(TDI)、聚四氢呋喃醚二醇(PTMG)、聚乙二醇(PEG)为原料，二月桂酸二丁基锡为催化剂，合成端异氰酸酯基聚氨酯预聚体，然后用己内酰胺作封闭剂与预聚体反应，得到封闭型聚氨酯作为导电胶基体树脂。采用红外(FTIR)和核磁(^{1}HNMR)等方法对预聚体及封闭聚氨酯进行了表征。封闭后的聚氨酯在室温下放置半年以上黏度没有明显变化。使用多种固化剂固化基体树脂，并测定其剪切强度，确定最佳固化剂为三羟甲基丙烷(TMP)。在基体树脂中添加固化剂、银粉、适量溶剂并搅拌均匀制得单组分导电胶，其中银粉最佳用量为 75wt%。

2. 通过 TDI、TMP 和少量 PEG（或 PTMG）进行缩聚，并与己内酰胺反应，制备封闭型 TMP-TDI 加成物作为导电胶基体。基体中添加银粉及固化剂，制备导电胶，并在其中添加气相二氧化硅。通过红外光谱、剪切强度和电阻率的测定等方法对产物进行了表征，结果表明，70℃下 TMP、TDI 的加成反应需要时间为 4～4.5h，与己内酰胺的封闭反应时间为 3～4h；银粉的质量分数为 75%时性能最好；加入少量二氧化硅能够提高导电胶的剪切强度，但电阻率会随之升高。

3. 将咪唑与各种金属卤化物反应，制备六种咪唑盐络合物，使用紫外可见吸收光谱对其进行了表征；以环氧树脂为基体，咪唑及六种咪唑盐络合物为固化剂，添加银粉及活性稀释剂制备一系列的单组分导电胶，并通过电阻率和剪切强度测定、DSC、黏度测定等方法对其性能进行了研究。咪唑作为环氧树脂导电胶的固化剂，最佳用量为 5phr；在 150℃下恒温固化 0.5h，除咪唑铜盐络合物外，

其他 5 种以咪唑盐作为固化剂的导电胶均有较高的剪切强度(大于 10MPa)；在环氧树脂中添加同比例的咪唑或咪唑盐及稀释剂，配制一系列环氧树脂体系，观察常温下黏度变化。与加入咪唑的固化体系相比，加入咪唑盐络合物的固化体系黏度变化显著较慢，其中以咪唑镍盐的效果最好，适合用于单组分环氧导电胶的固化剂，可明显提高室温下的储存期。

4. 以双氰胺作为主固化剂，咪唑、2-乙基-4-甲基咪唑(EMI)、6 种咪唑盐络合物为固化促进剂，添加银粉和稀释剂配制一系列单组分银粉导电胶。在 150℃下固化 0.5h，这些导电胶均有较高的剪切强度和低的电阻率。通过常温下的黏度测定比较，发现双氰胺体系的环氧树脂在常温下的储存期更长，尤其是咪唑镍盐和咪唑铜盐作为固化促进剂的体系，常温下放置 6 个月黏度无明显变化。

5. 以双氰胺为主固化剂、EMI 为固化促进剂的环氧树脂导电胶体系作为基础，研究了气相二氧化硅、消泡剂甲基硅油、偶联剂 KH-560 等助剂及双氰胺粉末粒径、银粉粒径、混合方式等对导电胶性能的影响。由剪切强度和电阻率数据可知，气相二氧化硅、消泡剂和偶联剂的加入都能够提高导电胶的剪切强度，它们的最佳用量分别为 3phr、1phr 和 2phr。随着双氰胺粉末粒径的减小，导电胶剪切强度增大，但对电阻率影响不大；银粉粒径增大，导电胶剪切强度增大，电阻率亦增大；与手动搅拌得到的导电胶相比，经过锥磨的导电胶的剪切强度明显提高。

6.本课题制得的单组分环氧导电胶，经过厂家点胶和背胶的实际测试，在粘结强度、储存期、电阻率、施工性能等方面，均达到工业应用要求，可在室温下储存运输，克服了美国和日本的进口导电胶必须在 0℃下运输和储存的缺点。

关键词：单组分导电胶　封闭型聚氨酯　潜伏型环氧树脂

Abstract

With advances in microelectronics and requirement of lead-free joint, more and more attentions have been paid to electrical conductive adhesives (ECAs), which illustrate a promising prospect of application and extension. One of the ECAs is one-part conductive adhesives. One-part ECAs consist of matrix, conductive fillers, curing agent and other additives. Compared with other kinds of ECAs, one-part ECAs have higher commercial values because of their convenience in construction. However, current ECAs still have some property limitations and challenges, including short pot life at room temperature and low adhesion strength. To solve the issues, a series of one-part ECAs were prepared with blocked polyurethane (PU) and epoxy resin as matrices respectively, Ag powder as conductive fillers.

1. Prepolymer of PU with isocyanate end groups was synthesized using TDI, PTMG, PEG as starting materials, dibutyl tin dilaurate as catalyst. Then the prepolymer was blocked by caprolactam to get blocked PU. Prepolymer and blocked PU were characterized by FTIR and ^{1}HNMR. The viscosity of blocked PU didn't increase apparently over half a year at room temperature. Several compounds were used as hardener to harden PU and shear strength was measured respectively. It was found that TMP was optimum curing agnet. Curing agent and Ag powder were added to blocked PU to obtain ECAs. The optimum mass fraction of Ag in ECAs was 75%.

2. The preparation and properties of one-part Ag-powder conductive adhesives which consisted of TMP-TDI adduct as matrix and TMP as curing agent were studied. TMP-TDI adduct was synthesized by TMP, TDI and PEG. Then the prepolymer was blocked by caprolactam to get blocked polyurethane. Curing agent, Ag powder and fumed silica were added to the polyurethane to prepare one-part conductive adhesives through agitating well. The products were characterized by FTIR, moreover, their shear strength and electrical resistivity were measured respectively. The results demonstrated that the addition reaction of TMP and TDI needed 4～4.5h,while the

blocked reaction needed 3～4h; The optimum mass fraction of Ag powder is 75%; Employing fumed silica to the conductive adhesive reinforced the shear strength and electrical resistivity.

3. Six imidazole salt complexes were synthesized and characterized by UV-Vis absorption spectra. The complexes and imidazole were used as curing agents to add to epoxy resin to prepare a series of ECAs. Electrical resistivity, shear strength of ECAs and viscosity of one-part epoxy resin were measured and DSC was used to investigate their properties. The optimum dosage of imidazole used as curing agent in ECAs based on epoxy was 5 phr (parts per hundreds of resin). After cured for 0.5h at 150℃, ECAs had high shear strength (more than 10MPa) with complexes as hardener except copper complex. When complexes were used as curing agent in epoxy, viscosity of epoxy increased more slowly than epoxy with imidazole. Epoxy with nickel complex had longest pot life, which was most suitable for ECAs as curing agent in the six complexes.

4. A series of matrices were prepared using epoxy resin as matrix, dicyandiamide as curing agent, imidazole, EMI and imidazole complexes as catalysts. Then Ag powder and diluent were added to matrices and the mixtures were agitated well to get a series of ECAs. The ECAs had high shear strength and low electrical resistivity after cured. A long pot life of matrices had been demonstrated through viscosity measuring. Especially epoxy with nickel and copper complex exhibited stable viscosity in 6 months at room temperature.

5. Additives such as Fumed silica, defoaming agent methyl silicone oil, coupling agent KH-560 were added into ECAs, which contained epoxy as matrix, DICY as hardener, EMI as catalyst. The influence of additives on ECAs' properties was investigated. The results demonstrated that additives increased the shear strength of ECAs. Their optimum dosages in ECAs were 3phr, 1phr and 2phr respectively. The influence of particle size of DICY powder and Ag powder, mixing methods was also studied. Shear strength increased when particle size of DICY decreased. If particle size of Ag powder increased, shear strength and electrical resistivity both increasd. Compared to ECAs agitated by hands, ECAs mixed by cone crusher had higher shear

strength.

6. One-part ECAs prepared in this paper, especially ECAs with epoxy as matrix, had been tested through dispensing and backing adhesives. All performances of ECAs, including adhesion strength, pot life, electrical resistivity, properties of construction, have met the requirement of the consumers excellently. The shortages of transporting and storing below 0℃ were overcomed in foreign products.

Keywords: One-part electrical conductive adhesives; Blocked polyurethane; Epoxy using latent hardener