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REVIEW

Electrically Conductive Adhesives with a Focus on Adhesives that Contain Carbon Nanotubes

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ABSTRACT: On the basis of an analysis of results presented in the literature, the currently existing knowledge about relationships between the microstructural and physical properties of hard coatings is discussed. Particular emphasis is placed on the role of microstructural features, such as grain boundaries, nonequilibrium structures, impurities, and texture, in controlling the film hardness. On the basis of an analysis of results presented in the literature, the currently existing knowledge of electrically conductive adhesives (ECAs) is discussed. Particular focus is placed on the results obtained with ECAs that contain carbon nanotubes (CNTs) as conductive fillers. The review is divided in curable ECAs based on epoxy resins, and noncurable conductive hot melts and pressure-sensitive adhesives based on thermoplastic polymers. More literature results were found for epoxy/conductive filler ECAs than for other adhesives. Confirming the assessments made in a book by Li et al., which refers to nanotechnologies in ECAs, we found that only a reduced number of articles allude to polymer/CNT ECAs. Our analysis of the results includes a study of the balance between the viscosity, immediate adhesion, solidification process, electrical conductivity, and mechanical properties of the adhesives. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: adhesives; conducting polymers; graphene and fullerenes; nanotubes

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INTRODUCTION

Few books, reviews, and briefings have been written with the objective of reviewing the state of the art in electrically conductive adhesives (ECAs).[1–12] Our analysis of these publications allows us to remark that the literature is focused to a great extent on adhesives constituted by an epoxy resin that provides physical and mechanical properties (adhesion, mechanical strength, and impact strength) and a metal filler, typically silver, that conducts electricity. Other conductive fillers, such as carbon black, graphite, graphene, and carbon nanotubes (CNTs), dispersed in other polymer matrices, such as silicone, polyamide, or polyurethane (PUR), are also discussed but in a very small proportion.

The information reported in these reviews refers mostly to epoxy-based ECAs with applications in the electronics industry, such as in interconnections in microelectronics, for instance, in integrated circuits. Other specific fields of epoxy-based ECAs, such as conductive inks, lithography, and metals protection, are also considered, whereas electrical conductive adhesives in other fields of industrial adhesion, such as widely used hot melts, and pressure-sensitive adhesives (PSAs), have been ignored in the reviews published so far.

Depending on their intended purpose, the required electrical conductivity of ECAs may vary from 10^{-2} to 10^{5} S/m; this allows the classification of these materials in the field of semiconductors and isolating conventional adhesives with conductivities below 10^{-10} S/m. Therefore, *electrical percolation*, threshold which is defined as the filler concentration at which the electrical conductivity increases sharply by orders of magnitude, is a basic requirement of ECAs. The conductive filler concentration should be higher than the percolation threshold; this indicates that conductive pathways span the macroscopic sample. Below the percolation threshold, electrons must travel through considerable amounts of insulating matrix between the conductive filler particles, whereas above the percolation concentration, electrons conduct predominantly along the filler and move directly from one filler particle to the next.[13,14]

However, in addition to the peculiarity of being semiconductor materials, ECAs should respond adequately to the physicochemical requirements reflected in Figure 1. The necessity of fulfilling all of the aspects implied in this scheme is certainly not considered in the aforementioned reviews, which are focused on the electrical properties and, to a lower extent, on the mechanical strength.

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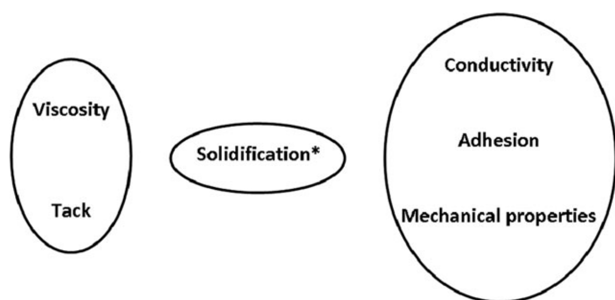

Figure 1. Physicochemical aspects involved in the ECAs. *Solidification is produced by curing, cooling, or solvent evaporation, depending on the adhesive type.

In view of the discussed remarks, we had three reasons for writing this review: (1) an analysis and comparison of ECAs based on different types of polymer matrices (thermosets, thermoplastics, and latexes) has not been presented in a review so far; (2) in the currently available reviews, the general requirements shown in Figure 1 are not considered as a whole, and (3) notwithstanding the enormous importance of CNT/polymer nanocomposites, no review focused on ECAs based on CNTs has been published up to this point.

The review is organized following the general scheme shown in Figure 2, with a focus on adhesives that contain CNTs.

EPOXY-BASED ECAs

As reflected in a considerable number of articles,[6,7,15–65] in the last 2 decades, epoxy-based ECAs have been developed for interconnections in electronic applications as an environmentally friendly alternative to traditional tin/lead solders. Another advantage is that epoxy-based solders can be used at higher temperatures. Anisotropic conductive films based on epoxies are used for flat-panel displays that have a lighter weight and lower consumption.

Conductive particles dispersed on a resin should have an adequate viscosity, which is not excessively low to avoid draining, and tacking or sticking capacity to fulfill the necessary conditions for an ulterior welding. After the dispersion is applied on the surface, the curing process will lead to solidification under the most favorable time and temperature conditions. The final product should have the electrical conductivity required for the established purpose and good final adhesion and mechanical properties. Epoxy resin provides adhesion to different substrates, mechanical strength, impact strength, and a high glass-transition temperature, as well as a relatively low curing temperature, whereas adequately dispersed conductive fillers give electrical conductivity to the system. The low viscosity of the system before curing facilitates the application processes, such as thermocompression, used in adhesive films.

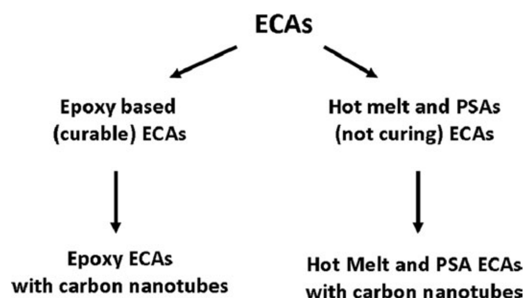

Figure 2. Roadmap of this article. The review focuses on ECAs with CNTs (in boldface).

An analysis of the literature on epoxy-based ECAs reflects that the works refer to some properties mentioned in Figure 1 but rarely report on the whole process starting from the viscosity to the mechanical properties. Yim et al.'s[16] article is an exception, because the viscosity, wettability, and electrical and mechanical properties of epoxy/silver and epoxy/tin ECA formulations were discussed. A great majority of these published articles refer to epoxy ECAs with metal fillers,[4–6,15–42] predominantly silver, but also gold, nickel, and copper.

The compromise between electrical conductivity and adhesion is often mentioned because a high filler content, which is necessary to reach an adequate conductivity, normally implies poor adhesion.

Notwithstanding its importance, the rheological behavior of ECAs based on epoxy is scarcely treated in the literature. Gilleo[4] referred to the thixotropic behavior of the pastes that constitute the adhesive before curing, and Jia et al.[41] reported that high loading levels lead to high viscosities and thus reduce the sedimentation of Ag particles during curing. On the other hand, Yim et al.[16] investigated the rheological response of various ECAs employed for electronic packaging and showed that the viscosity had a significant influence on the flow–coalescence–wetting behavior.

The effect of conductive particles on the curing process has not been granted special attention by researchers, as indicated by the reduced number of articles that have discussed this aspect. Gao et al.[36] observed that the increased viscosity of epoxy due to curing could prevent the agglomeration of silver particles. The curing conditions were also correlated with the composition of investigated ECAs by Uddin et al.[18] The effect of curing on the electrical conductivity of epoxy-based ECAs was reported by Klosterman et al.,[31] who pointed out a remarkable conductivity increase during curing. It was hypothesized that this conductivity enhancement was due to silver particles packing during the decrease in viscosity at a very early stage of the curing process. A different explanation, based on shrinkage associated with curing, was offered by Liu et al.[25] for the conductivity increase in their epoxy/silver ECAs.

The irruption of intrinsically conductive polymers at the beginning of the millennium brought about some advancement in the field of ECAs, as highlighted in Chapter 8 of Li et al.'s[1] book, although the results obtained so far are less relevant than could be expected. Mir and Kumar[43] and Sancaktar and Liu[44] reported on the electrical conductivity and adhesive joint resistance of epoxy ECAs that included, respectively, electrically conducting polyaniline and polypyrrole.

On the other hand, the development of nanotechnology has led to alternatives to traditional metal fillers to obtain epoxy-based

Table I. Summary of the Results Found in the Literature for Epoxy/CNT ECAs

Authors	CNT characteristics	Percolation threshold	Maximum electrical conductivity	Adhesion and other properties
Jing and Lumpp[53]	Unspecified CNTs	3 wt %	1.5×10^5 S/m with 3 wt % CNTs	With the addition of 3 wt % CNTs, the shear strength remained similar to that of the pure epoxy. The thermal diffusivity was three times higher.
Li et al.[65]	Epoxy filled with Ag and unspecified CNTs	—	10^5 S/m with 66.5 wt % Ag and 0.27% CNTs	—
Wu et al.[17]	Unspecified CNTs coated with silver	—	4×10^5 S/m with 28 wt % CNT-Ag	Similar shear strength for coated and uncoated CNTs
Ma and coworkers[55,56]	Unspecified CNTs decorated with silver	0.1 wt %	3×10^3 S/m with 0.5 wt % CNT-Ag	The flexural strength and thermal conductivity were improved with the addition of CNT-Ag.
Jiang et al.[47]	Unspecified CNTs	—	The conductivity increased 20% when 0.03 wt % CNTs were added to pristine epoxy	The thermal conductivity increased 17% with the addition of 0.03 wt % CNTs. The coefficient of thermal expansion decreased.
Tang et al.[64]	Unspecified CNTs	—	2.2×10^4 S/m, obtained with a postcuring treatment	Peeling strength (4 N/mm) was claimed to be excellent.

ECAs. Several articles refer to the enhancement of the electrical conductivity in nanosilver-filled epoxy adhesives[45–47] and in epoxy adhesives filled with silver nanowires and silver nanorods.[45,48] SiO_2 nanoparticles and silane coupling agents can prevent the agglomeration of copper conductive particles and allow a better adhesion strength and enhanced electrical conductivity, as reported by Zhao et al.[42] A novel route was developed by Lin et al.,[49] who reported on the elaboration of ECAs with epoxy filled with silver-plated nanographite fillers. The use of conductive particles derived from graphite dispersed in an epoxy matrix has also gotten some attention. Almost a decade ago, Novák and Krupa[50] investigated ECAs based on epoxy and PUR resins filled with graphite; they observed that 22 vol % graphite was necessary to achieve electroconductive adhesives, but only values of the conductivity relative to the polymer matrices were reported. Better results were obtained with carbon nanocones (stacked conically folded graphene sheets) dispersed in epoxy, because conductivities of the order of 0.1 S/m were obtained with only 2 vol %.[51]

Within this context, the use of CNTs to obtain epoxy-based electrically conductive nanocomposite adhesives has gotten relatively little attention in the literature as is reflected, for instance, in the reduced number of references alluding to CNTs in Li et al.'s[1] book. The corresponding articles on this subject are discussed later.

ECAs BASED ON EPOXY/CNT NANOCOMPOSITES

The main advantage of CNTs compared with other conductive fillers is their excellent electrical conductivity, nanoscopic size, and high aspect ratio, which facilitates the formation of a network that allows electron transport along the CNTs. The characteristics of CNTs include the origin of a very low electrical percolation threshold value of polymer/CNT systems, which can be eventually lowered because of the hopping/tunneling effect between CNTs.[60–62] In the review article of Bauhofer and Kovacs,[63] a list of the percolation threshold values of dispersions of pure and functionalized single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNT) in different polymer matrices is reported. This list of values was analyzed with a very illustrating percolation data plot in a recent article of Ma et al.[56] The following conclusions could be made: (1) overall, similar percolation threshold values were obtained with SWCNTs and MWCNTs; (2) a wide range (more than 2 decades) of threshold values were obtained with each polymer matrix, depending on the quality of CNT dispersions, and (3) epoxy resins are the only matrices that eventually allow percolation thresholds below 0.01 wt % CNTs.

Few articles refer directly or implicitly to the electrical percolation of ECAs based on epoxy/CNT nanocomposites. A summary of the reported results is presented in Table I. Jing and Lumpp[53] investigated the effect of CNT loading in an epoxy resin, reporting a volume resistivity of 6.4×10^{-4} Ω cm, which corresponds to a conductivity of 1.5×10^5 S/m. According to the authors, this value is comparable to the best commercial metal-particle-filled ECAs and to metal solder joints. The evaluated percolation threshold of their epoxy/MWCNT ECAs was around 3 wt %, which is a very high value according to the values reported in the review article of Bauhofer and Kovacs.[63] An electrical conductivity of 2.2×10^4 S/m was reported by Tang et al.,[64] but the CNT concentration necessary to reach this conductivity value was not indicated. On the other hand, in Hongjin et al.,[52] the contact resistances (inversely proportional to the electrical conductivity) of an epoxy-based adhesive without CNTs and with 0.03 wt % CNTs were compared; they showed that the electrical conductivity was only increased by 14% with CNTs. This indicated that this concentration was below the percolation threshold value, and the authors claimed that the electrical

conductivity enhancement was due to the high thermal conductivity of the CNTs. Actually, Kwon et al.[54] reported a 50% increase in the thermal conductivity of an epoxy-based ECA when the resin was filled with 1 wt % MWCNTs, but no electrical conductivity values were presented. The possibility of a synergy between the aspect ratio of CNTs and the electrical conductivity of silver has also been considered.[55,59,65] As an example of the effectiveness of the addition of CNTs to epoxy-based ECA classical formulations, it has been found that the electrical conductivity of an adhesive filled with 66.5 wt % Ag passed from 10^{-2} to 10^5 S/m after the addition of 0.27 wt % CNTs.[65] A more sophisticated chemical plating method was used by Wu et al.[59] to prepare silver-coated CNTs that were dispersed in an epoxy resin to obtain ECAs. Their results show that at a filler content of 28 wt %, the ECAs filled with the coated CNTs presented the highest conductivity (4×10^5 S/m) compared to noncoated CNTs, which had a conductivity 10 times lower with 31 wt % CNTs. For their part, Ma et al.[55] used the term *CNT decoration* to define the presence of silver nanoparticles on the surface of MWCNTs; this was accomplished by a reducing reaction of silver ions with dimethylformamide. The authors observed that with 0.1 wt % filler, the electrical conductivity increased four orders of magnitude when Ag nanoparticles were on the surface of the CNTs.

One pertinent question related to the solidification process of the middle block of Figure 1 was the eventual variation of the electrical conductivity when the curing process of the epoxy took place. In the case of ECAs that contain CNTs, the variation of the electrical conductivity during the curing process has practically not been considered in the literature. Only Tang et al.[64] referred to this subject, studying the influence of postcuring on the electrical conductivity: They found that the conductivity increased after postcuring. In any case, this subject has also been scarcely treated for epoxy/CNT nanocomposites in general, and contradictory results have been reported. A conductivity enhancement during curing was reported by Sandler et al.[66] for MWCNT-reinforced epoxy nanocomposites; this was associated by the authors with a spontaneous reaggregation of the CNTs in the curing process. The opposite trend (a conductivity decrease during curing) was observed by Chapartegui et al.,[67] who indicated that MWCNTs aggregates were already present in the dispersion and were not formed in the curing process. Currently, it is considered that a reduction in the electrical conductivity can be due to factors such as (1) a distortion of the nanotube network as a result of shrinkage during the crosslinking process and (2) the number of charge carriers (unreacted epoxy prepolymer and amine molecules) that contribute to ionic conductivity being reduced as crosslinking takes place.

Also linked to the scheme of Figure 1, one can ask how the curing process (solidification in Figure 1) may be affected by the presence of CNTs, a question that has not been investigated in the case of ECAs so far. In the more general field of epoxy/CNT nanocomposites, viscoelastic and dielectric experiments have demonstrated that the presence of MWCNTs accelerates the temperature-activated curing in comparison with pure epoxy resin.[67–73] This result was attributed to the presence of impurities that activate the early stage of curing, although the explanation of this behavior has not yet been totally clarified.

The improving effect of CNTs on the electrical conductivity of ECAs should not be at the expense of the other properties of the adhesives detailed in Figure 1, such as viscosity and tack, and the adhesion and mechanical properties. Notwithstanding that the viscosity of the epoxy prepolymer (before curing) is a factor that affects the degree of dispersion of CNTs, only partial studies have been carried out so far, for instance, to explain the difficulties in dispersing CNTs in the most viscous epoxy prepolymer[53,54] or related to the formation of undesirable voids.[54,56] The viscosity change with exposure time, which allows to evaluate the pot life of the adhesive, was also investigated in one case.[64]

Certainly, these technical problems are not specific of epoxy/CNT ECAs because the elaboration of any performing epoxy/CNT nanocomposite is based in an adequate CNT dispersion before the curing process. Surprisingly, there are not many sound articles on the rheology of CNT dispersions in epoxy prepolymer systems in general. Some researchers have studied the dynamic viscoelastic behavior of these dispersions in the linear regime and have shown that a physical network is formed, giving rise to the so-called *rheological percolation*.[74,75] The nonlinear viscosity of CNT dispersions in epoxy prepolymers in continuous flows has also been scarcely treated.[61,74,76,77] The results indicate that under continuous shear flow, the physical network is destroyed, giving rise to a viscoplastic and shear thinning behavior, which is reflected in the viscosity data of Figure 3. A considerable viscosity increase with CNT concentration was observed, but interestingly enough, this effect was significantly reduced as the shear rate increased; this is a favorable result for processes that can involve relatively high shear rates, such as coating or surface covering during the application of ECAs.

In addition to an adequate electrical conductivity, ECAs based on epoxy and CNTs should have good final adhesion and mechanical properties. This was contemplated in particular for the aforementioned ECAs based on epoxy and CNTs decorated with silver nanoparticles. It was observed that the flexural modulus

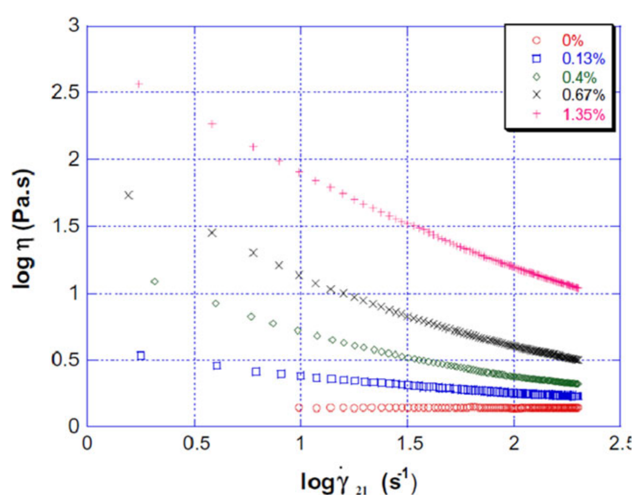

Figure 3. Viscosity (η) as a function of the shear rate at 23°C for the pure epoxy prepolymer and epoxy/MWCNT dispersions (reproduced from ref. 61). Similar results were shown in Figure 4 in ref. 76. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and flexural strength increased with increasing CNT content; nevertheless, the strengths of ECAs containing silver on the surface of CNTs were higher than those of pristine CNTs. A double benefit of silver-coated CNTs on both properties, the electrical conductivity and mechanical strength, was also observed by Wu et al.[59] because the authors remarked that the adhesive with the highest conductivity showed the highest shear strength as well. Ma et al.[55] also observed enhancements in the electrical conductivity and flexural strength when CNTs were added to the epoxy matrix, and according to Tang et al.,[64] excellent peeling properties where obtained with their ECAs based on epoxy and CNTs.

Actually, for epoxy/CNT nanocomposites, improved strengths with respect to pure epoxy have been reported;[54,78–85] this could have been due to the eventual formation of covalent bonds between CNTs and the epoxy matrix. In this regard, Kwuon et al.[54] reported an increase in the pull strength of epoxy/CNT ECAs when *m*-phenyenediamine grafted MWCNTs were used. Significantly, MWCNTs have been used for the sole purpose of increasing toughness and strength in nonelectrically conductive epoxy adhesives.[58] In contrast to the exposed general trend, Jing and Lumpp[53] observed a 20% reduction in the shear strength of an ECA that contained 0.8 wt % unmodified MWCNTs with respect to the strength of the pure epoxy matrix. In any case, this was not a bad result because, as the authors remarked, with conventional metal-filled ECAs, the strength reduction is more than 70%.

In Table I, the adhesion and other properties of the investigated epoxy/CNT ECAs are included in addition to the electrical conductivity.

ECAs THAT DO NOT CURE: HOT-MELT ADHESIVES AND PSAs

In contrast to epoxy-based adhesives, which undergo a curing process to achieve welding, noncuring adhesives get their permanent adhesion by cooling or solvent casting. This is the case in thermoplastics, latexes, and solutions produced to be used as hot-melt adhesives or contact adhesives, including PSAs. Compared to epoxy-based ECAs, noncuring ECAs have aroused much less attention in the literature. Apart from noncuring ECAs based on CNTs,[86–91] which are contemplated in a later section, two articles have treated electrically conductive hot melts and PSA adhesives. In particular, Lee et al.[92] studied the effect of nanosilver particles on the electrical conductivity of poly(vinyl acetate) emulsions with potential application as ECAs. They reported a conductivity of 5×10^5 S/m and observed that increasing the temperature helped to form necks between particles and improved the conductivity. For their part, Zimmerer et al.[93] developed a conductive additive based on an intrinsically conductive polymer [sodium sulfosuccianate coupled poly(ethylene glycol)] for hot-melt adhesives. The highest obtained conductivity was 0.9 S/m, which according to the authors, was useful for hot-melt adhesives and for antistatic plastic coatings.

ELECTRICALLY CONDUCTIVE HOT MELTS, PSAs, AND OTHER NONCURING ADHESIVES WITH CNTs

Although the number of articles on hot-melt adhesives based on polymer/CNT systems is very limited, there is currently increasing interest in these materials. For instance, ARKEMA nowadays produces a commercial master batch of MWCNTs dispersed in a polyamide claimed to be used to manufacture conductive hot-melt adhesives because of its good balance among viscosity, adhesion, and conductivity.[94] As is discussed previously for ECAs based on epoxy/CNT nanocomposites, this balance and the overall conditions expressed in Figure 1 should be considered in the analysis of this type of adhesive. The abundant literature on thermoplastics filled with CNTs can help one understand the expected viscosity, electrical conductivity, and mechanical properties of hot-melt ECAs. For instance, it is well known that increasing the concentration of CNT leads to the enhancement in the electrical conductivity and, in general, to an improvement in the mechanical properties; on the other hand, the viscosity increases, which can cause eventual processing troubles. Representative articles of this behavior include refs. 95–99. However, other crucial aspects of polymer/CNT nanocomposites linked to their potential application as ECAs, such as immediate adhesion (tack) and welding properties, have been disregarded. As an exception, the viscoelastic properties and tack (immediate adhesion) results have been correlated in PUR/MWCNT nanocomposites with conductivities close to 10^{-2} S/m and viscosities similar to that of the PUR matrix, which is actually a hot-melt adhesive.[100] The elastic modulus (G') and loss modulus (G'') values of these PUR/MWCNT nanocomposites as a function of the frequency obtained in the linear dynamic viscoelastic regime are presented in Figure 4. A significant alteration with respect to the response of the thermoplastic elastomer (TPU) PUR was observed for the highest MWCNT concentrations because the elastic modulus showed a plateau at low frequencies, with $G' > G''$, which was associated with a combined MWCNT–PUR network.

The role played by this combined network in probe–tack experiments was remarkable and gave rise to a fibrillation mechanism during debonding tests. This was observed as a plateau in stress–strain curves, as shown in Figure 5. This produced an enhancement in the stress–strain area and brought about

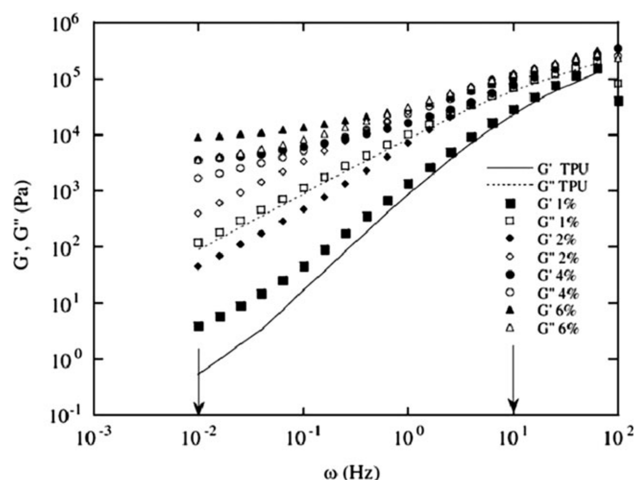

Figure 4. G' and G'' values as a function of the frequency (ω) for the PUR sample and PUR/MWCNT electrically conductive nanocomposites of the indicated concentrations (reproduced from ref. 100).

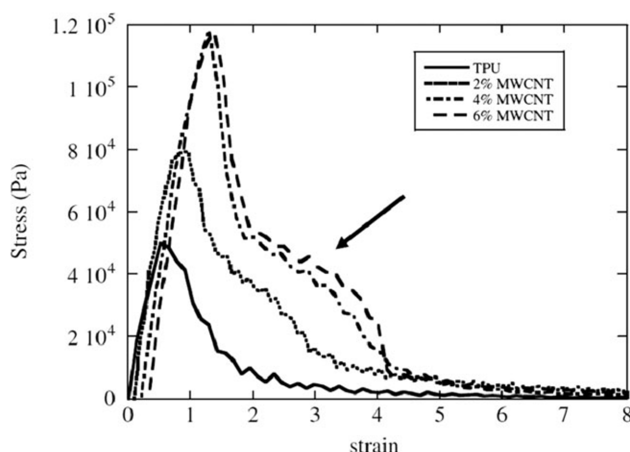

Figure 5. Stress–strain curves obtained in the probe–tack (debonding) experiments with the PUR and PUR/MWCNT electrically conductive nanocomposites. The arrow indicates the stress–strain plateau due to fibrillation (reproduced from ref. 100).

energies of adhesion that increased from 3.3 J/m^2 for pure PUR to 7.84 J/m^2 for 2% MWCNTs and 10.79 J/m^2 for 4% MWCNTs.

Some hot-melt adhesives are semicrystalline polymers, such as polyamides, polyolefins, and PURs, and, therefore, crystallization during cooling plays an important role in the adhesion and mechanical properties. In the majority of the cases, CNTs produce a nucleating effect in semicrystalline polymers and give rise to higher crystallization degrees and crystallization rates; this can improve the strength at room temperature and the welding rate during cooling.[101–116] These benefits were highlighted by Fernández et al.[117] for ECAs based on PUR/MWCNT nanocomposites.

Similar to the case of ECAs based on curing epoxy resins, the question of variation in the electrical conductivity during the solidification process of electrically conductive hot melts should be confronted. The hot melt is applied in the molten state, and permanent adhesion is produced on cooling below the crystallization temperature. Therefore, from a practical point of view, the electrical conductivity that is relevant is the conductivity of the adhesive after it is subjected to this treatment. This implies a study of the evolution of electrical conductivity from the molten state to the solid state as the polymer matrix crystallizes. The published literature reflects contradictory results on the variation of the electrical conductivity in semicrystalline-polymer-CNT-based nanocomposites. A conductivity increase during crystallization was observed for CNTs dispersed in PUR,[62] ethylene vinyl acetate copolymer,[118] polystyrene,[118] polypropylene–ethylene copolymer,[119] and poly(vinylidene fluoride),[120] whereas in other cases, such as ultra high-molecular-weight polyethylene,[121] polyethylene,[122] and polypropylene,[123] an electrical conductivity decrease has been reported. Interestingly, the results of the aforementioned PUR/MWCNT ECA nanocomposite indicated a considerable increase in the electrical conductivity (more than one order of magnitude) during crystallization for MWCNT concentrations above the critical percolation threshold value (1 wt %).[62]

The case of ECAs based on a thermoplastic amorphous matrix, poly(methyl methacrylate), filled with silver flakes and CNTs was considered by Wu et al.[124] The system responded to the general characteristics of a hot-melt ECA, but the authors did not explicitly mention it. Similar to the case of the addition of CNTs to an epoxy-based ECA that contained silver,[65] as mentioned previously, the addition of 2 wt % MWCNTs to an ECA that contained 50 wt % silver increased the electrical conductivity up to a value of 6.6×10^5 S/m. This very appreciable electrical conductivity was obtained with MWCNTs (but not with SWCNTs) at the optimum settings of processing temperature and pressure.

Also, combining different conductive fillers, Tung et al.[88] obtained electrically conductive glues through the synergistic assembly of graphene oxide (GO), SWCNTs, and aqueous solutions of poly(3,4-ethylene–dyoxithiophene) (PEDOT)–poly(styrene sulfonate) (PSS). These glues were reported to be suitable for connecting subcells in a tandem photovoltaic device and for batteries and fuel cells because they were capacitance-active and stable in acidic and neutral aqueous electrolytes. The presence of GO facilitated the dispersion of SWCNTs in the PEDOT–PSS solution and formed a stable suspension, which turned into a hydrogel for combinations of 0,5, 1, and 1.5 wt % SWCNTs, GO, and PEDOT–PSS, respectively. The formation of a network comprised of GO sheets and SWCNTs inside PEDOT–PSS, identified by scanning electron microscopy images of the dried glue, gave rise to a viscosity increase. As shown in Figure 6,[88] the shear stress–shear strain curves obtained with different formulations used to glue two strips of poly(ethylene terephthalate) showed that the GO–SWCNT–PEDOT–PSS combination gave the best mechanical results. The obtained high electrical conductivity (2.4×10^3 S/m) of the ternary glue was due to the presence of SWCNTs.

Hot-melt adhesives should be tacky in the molten state and should bring permanent welding when they cool to room temperature, whereas PSAs, like self-stick tape, are applied and used

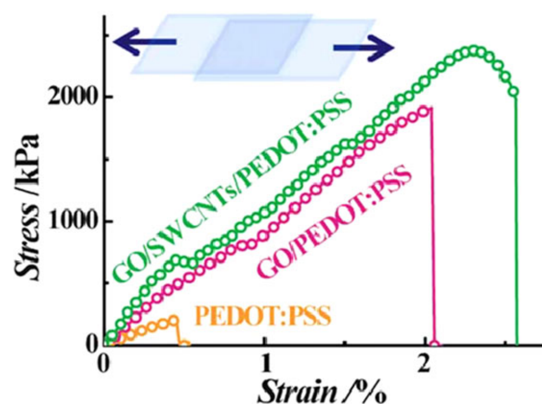

Figure 6. Stress–strain curves measured by the pulling of two PET strips glued by PEDOT–PSS, GO–PEDOT–PSS, and GO–SWCNTs–PEDOT–PSS electrical conductive adhesives. An improved mechanical response was observed when the SWCNTs were added (see text; reproduced from ref. 87). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

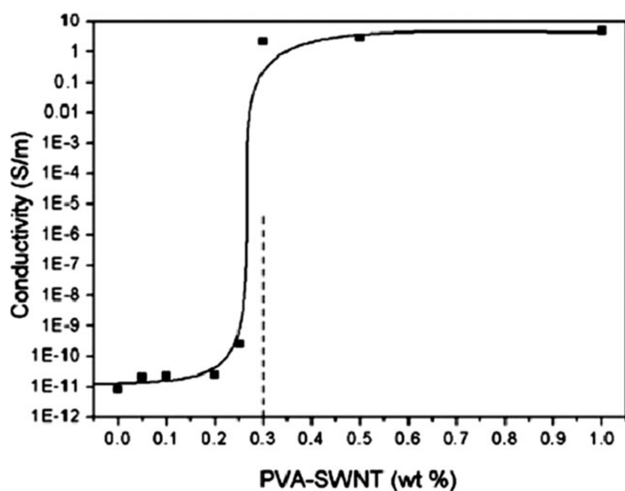

Figure 7. Electrical conductivity as a function of the PVA–CNT concentration showing a percolation threshold of 0.3 wt % (reproduced from ref. 89).

typically at room temperature, so they should have a permanent tack and peel adhesion. The compromise between electrical conductivity, viscosity, tack, and peel adhesion is difficult to reach in electrically conductive PSAs because the addition of CNTs will normally cause an unsuitable viscosity increase linked to a deterioration of tack. So far, the number of articles on electrically conductive PSAs is very limited, and to our knowledge, no commercial development is yet available. One interesting route, based on a poly(butyl acrylate) (PBA) latex, was proposed several years ago by Wang et al.[89] The electrical conductivity was achieved with SWCNTs that were functionalized with poly(vinyl alcohol) (PVA); this rendered them dispersible and stable in water. The PVA–SWCNT particles were blended with the PBA latex via sonication and provided the electrical conductivities that are presented in Figure 7. The electrical conductivity increased by 10 orders of magnitude (up to ~10 S/m) between concentrations of 0.25 and 0.30 wt % PVA–SWNTs. Also, the probe tack results showed that the addition of 0.3 wt % PVA–SWNTs yielded the optimum tack properties with an adhesion energy that practically doubled the value of PBA latex. Another interesting property, claimed by Wang et al.,[89] was the optical clarity of the adhesives, a property that is out of the expectations of ECAs that contain silver. Recently, Czech et al.[86] employed CNTs and nano carbon black fillers dispersed in a PBA matrix (which is an acrylic PSA) to produce electrically conductive PSAs. An electrical conductivity close to 5×10^3 S/m was reported with 25 wt % carbon black and 20 wt % CNTs, but the authors showed that the addition of these fillers reduced the tack and peel adhesion with respect to the PBA matrix.

CONCLUSIONS

In the last 2 decades, a considerable number of articles have been published on the development of epoxy-based ECAs for interconnections in electronic applications. A great majority of these publications refer to epoxy ECAs filled with silver, but other metals, like gold, nickel, and copper, are also considered. The compromise between the electrical conductivity and adhesion is mentioned in the articles, but practically no attention is paid to the effect of conductive particles on curing, even though this is a crucial process in epoxy adhesives.

The development of nanotechnologies has opened the door to new ECAs, such as nanosilver-filled epoxy adhesives, epoxy adhesives filled with silver nanowires and silver nanorods, and ECAs based on epoxy filled with silver-plated nanographite.

On the other hand, the main advantages of CNTs are their excellent electrical conductivity, nanoscopic size, and high aspect ratio, which facilitate the formation of a network that allows electron transport along the nanotubes. However, the use of CNTs to obtain epoxy-based electrically conductive nanocomposite adhesives has garnered relatively little attention in the literature. Only six articles give results on the electrical conductivity and adhesive properties of epoxy/CNT systems. The very low electrical percolation threshold values reported for epoxy/CNT nanocomposites are not reflected in epoxy/CNT ECAs because only two articles allude to this point. The maximum electrical conductivity obtained in an epoxy adhesive filled with pristine CNTs was 1.5×10^5 S/m with a 3 wt % CNT concentration; this is comparable to the best results obtained with much higher silver concentrations. Two clearly positive aspects of epoxy/CNT ECAs deserve to be mentioned: (1) the adhesion strength of ECAs is similar to that of pure epoxy, and (2) the thermal conductivity increases with CNTs and redounds to a lower coefficient of thermal expansion.

Thermoplastics, latexes, and solutions produced to be used as hot-melt adhesives, or PSAs, get their permanent adhesion by cooling or solvent casting. Compared to epoxy-based ECAs, noncuring ECAs have aroused much less attention in the literature: In our research, we counted only six articles, with four of them reporting on ECAs that contained CNTs. Classical metal conductive fillers, such as silver, employed in epoxy-based ECAs are only mentioned in one of the articles (silver mixed with CNTs). Instead, nanosilver particles, an intrinsically conductive polymer [sodium sulfosuccianate coupled poly(ethylene glycol)], GO, MWCNTs (in one case mixed with carbon black), and SWCNTs were used in combination with thermoplastics, such as PUR, poly(methyl methacrylate) and PBA, and latexes. Overall, an effort was made in these studies to investigate the balance between the tack, electrical conductivity, and mechanical properties of the adhesives.

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