APARATURA
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Acrylic pressure-sensitive adhesives modified with silver nanoparticles

ZBIGNIEW CZECH[1], ROBERT PEŁECH[1], AGNIESZKA KOWALCZYK[1], LU SHAO[2], YONG-PING BAI[2]

[1] INSTITUTE OF CHEMICAL ORGANIC TECHNOLOGY, WEST POMERANIAN UNIVERSITY OF TECHNOLOGY, SZCZECIN, POLAND

[2] SCHOOL OF CHEMICAL ENGINEERING AND TECHNOLOGY, STATE KEY LABORATORY OF URBAN WATER RESOURCE AND ENVIRONMENT (SKLUWRE), HARBIN INSTITUTE OF TECHNOLOGY, CHINA

ABSTRACT

Acrylic pressure-sensitive adhesives (PSA) are generally considered as non electrical conductive materials. The electrical conductivity is also incorporated into acrylic polymer after adding of electrical conductive additives like silver nanoparticles. After addition of electrical conductive silver nanofiller, the main and typical properties of pressure-sensitive adhesives such as tack, adhesion and cohesion are deteriorated. This study is the first trial which reveals that the acrylic self-adhesive basis must be synthesised with ameliorated initial performances like high tack and excellent adhesion. Currently, the electrical conductive solvent-borne acrylic PSA containing silver nanoparticles are not commercially available on the market. They are promising materials which can be applied for the manufacturing of diverse technical or medical high performance self-adhesive products, such as broadest line of special electrically conductive sensitive tapes.

Poliakrylanowe kleje samoprzylepne modyfikowane nanocząstkami srebra

STRESZCZENIE

Poliakrylanowe kleje samoprzylepne są generalnie uważane za materiały nie przewodzące prądu elektrycznego. Przewodnictwo elektryczne można osiągnąć poprzez dodatek do kleju samoprzylepnego przewodzących prąd elektryczny nanocząstek srebra. Po dodaniu napełniacza nieorganicznego przewodzącego prąd elektryczny typowe właściwości klejów samoprzylepnych, takie jak tack (lepność) oraz adhezja ulegają pogorszeniu. Niniejsza praca przedstawia konieczność stosowania jako matrycy polimerowej modyfikowanych klejów samoprzylepnych o dużej lepności oraz dużej adhezji przed dodatkiem przewodzącego prąd elektryczny napełniacza. Obecnie w sprzedaży nie spotyka się komercyjnych klejów samoprzylepnych przewodzących prąd elektryczny. Otrzymane w wyniku badań poliakrylanowe kleje samoprzylepne przewodzące prąd elektryczny mogą być stosowane do wytwarzania wysokowartościowych materiałów samoprzylepnych, zarówno natury technicznej jak i do zastosowań medycznych.

1. INTRODUCTION

The development in the area of electronic conductive polymers with a high electronic conductivity was award of the Nobel Prize for Chemistry in 2000 to Alan Heegre, Alan MacDiarmid, and Hideki Shirakawa. A variety of organic conducting polymer materials has now been developed for applications ranging from electromagnetic shielding and other applications in the electronic industry. A number of synthetic routes have been developed for the preparation of conjugated polymers. The diversity has been driven by the desire to examine many different types of conjugated polymers like polyacetylenes, polyphenylenes, polypyrroles, polythiophenes, poly (arylene vinylenes), and polyanilines and attempts to improve material properties. These six primary classes of conjugated polymers have been shown to exhibit high levels of electrical conductivity in the doped state. In addition a number of multicomponent materials, usually polymer blends and composites have been prepared in which at least one of the components is a conducting polymer [1-3].

The key feature of the electrically conductive organic polymers is the presence of conjugated bonds with π-electrons delocalized along the polymer chains. In the undopted form, the polymers are either insulating or semiconducting with a large band gap. The polymers are converted to the electrically conductive or doped forms via oxidation or reduction reactions that form delocalized charge carriers. Charge balance is accomplished by the incorporation of an oppositely charged counter ion into the polymer matrix. The conductivity is electronic in nature and no concurrent ion motion occurs in the solid state. Most applications of conducting polymers utilize their electronic properties, but some (eg. battery or sensor electrodes) involve their ionic properties [4-5].

However, these conjugated polymers are not suitable for pressure-sensitive adhesive films and their electrical conductivity is too low to be applied for a lot of important and typical applications in electronic industry (Fig.1) [6].

The addition of conductive fillers such as metal particles (copper, aluminum), special d modified carbon black, carbon fibers, metalized glass spheres and fibers allow the development of electrically conductive polymers with electrical conductivity between 10^{-2} and 10^{2} S/cm. This relatively high conductivity is the result of percolation of conducting filler particles in an insulating matrix or tunneling between the particles [7]. Electrically conductive pressure-sensitive adhesives are not commercially available on the market. They can be utilized for the manufacturing of diverse technical self-adhesive products, such as broadest line of electrically conductive sensitive tapes. It is well known that acrylic pressure-sensitive adhesives are generally considered as non electrical conductive materials. There is the pratical requirments for the development of PSA including special suitable self-adhesive polymers and their modification through adding of electrical conductive fillers. From the evaluated PSA, the best performances were achieved using acrylic PSA [8-11].

Electronic packaging plays an increasingly important role in modern electronic industry. In electronic packaging, interconnecting techniques of chips on substrate or printed circuit board restrict the miniaturization of electronic products. Normally, high performance conductive adhesives were designed by

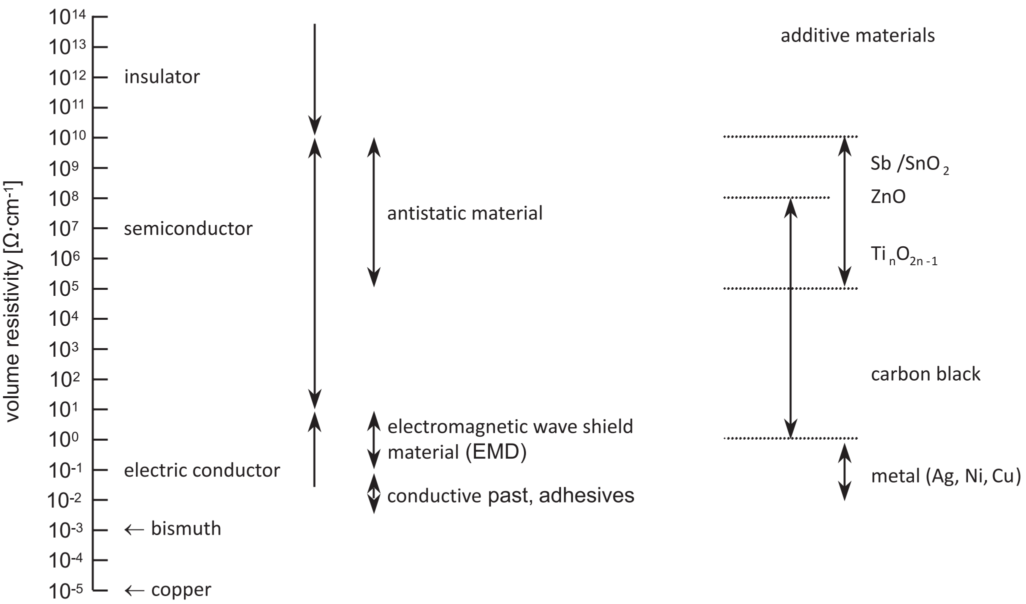


Figure 1. Electrically conductivity of diverse materials

combining the thermosetting resin and the efficient electrically conductive fillers [12]. One of the most effective techniques used to improve the electrical conductivity of polymers is the incorporation of conductive fillers in the polymer matrix. The most popular electrically conductive filler is silver due to its moderate cost and superior conductivity [13-14].

2. EXPERIMENTALS

2.1. Synthesis of acrylic PSA

The solvent-borne acrylic PSA as a basic polymer for electrically conductive PSA were synthesized in ethyl acetate with 50 wt.% polymer content by using of 50 wt.% 2-ethylhexyl acrylate, 45 wt.% butyl acrylate and 5 wt.% acrylic acid at presence of 0.1 wt.% radical starter AIBN at temperature of 78°C. All components were available from BASF.

2.2. Modification of synthesized acrylic PSA

The synthesized acrylic PSA was modified using 30 wt.% resin Dertophene T115 (DRT) and 10 wt. % resin Tragum 2331WS (Tramaco) and crosslinked with 0.4 wt.% titanium acetylacetonate (DuPoint). The properties of filler-free unmodified and modified acrylic PSA were demonstrated in the Table 1.

2.3. Addition of electrical conductivity fillers

The described trials were conducted using silver nano-filler in amounts between 3 wt.% and 40 wt.% with reference to polymer content. The silver nano-filler were dispersed into the adhesive solution using a dissolver at about 9000 rpm. Naturally, the addition of such fillers degrades the adhesive properties of the material, such as the tack and peel adhesion.

2.4. Measurement of PSA properties

The solvent-borne acrylic PSAs after modification using resins and later modified with silver nanoparticles are coated directly with 60 g/m^2 on a polyester film and after drying for 10 min at 105°C in drying canal. The typical properties of PSA such as tack, adhesion and cohesion and the influence of conductive fillers concentration on these adhesives properties were determined by standard A.F.E.R.A. (Association des Fabricants Europeens de Rubans Auto-Adhesifs) procedures. Exact details can be found in AFERA 4015 (tack), AFERA 4001 (peel adhesion), and AFERA 4012 (shear strength).

2.5. Electrical conduction properties

The electrical conductivity of a material, which is the inverse of its specific resistivity, is a measure of a material´s ability to transport electrical charge. The resistivity and conductivity are intrinsic properties of the material. If, independent of the sample dimensions, unlike resistance that depends on sample size. Electrical conductivity is commonly measured in units of S/cm. The most common method of measuring conductivity is known, described in a lot of technical literatures and international standardized. Surface resistivity is determinates according to DIN 53482 method.

3. RESULTS AND DISCUSSION

The main properties of the filler-free unmodified and modified basic acrylic PSA such as tack, adhesion and cohesion are shown in Table 1.

After addition of resins 30 wt.% Dertophene T115 and 10 wt. % resin Tragum 2331WS and 0.4 wt.% crosslinker titanium acetylacetonate, the adhesive-

Table 1. Properties of basic and modified acrylic PSA

Basic acrylic PSA					Modified acrylic PSA				
Tack	Adhesion		Cohesion		Tack	Adhesion		Cohesion	
	20°C	70°C	20°C	70°C		20°C	70°C	20°C	70°C
32.8 N	38.7 N	21.6 N	80 N	40 N	40.1 N	44.7 N	14.5 N	60 N	16 N

Table 2. Important adhesiveness and cohesiveness properties of acrylic PSAs containing electrically conductive silver nanoparticles

Concentration of silver nanoparticles [wt.%]	Tack [N]	Adhesion [N]		Cohesion [N]	
		20°C	70°C	20°C	70°C
free	40.1	44.7	14.5	60	16
3	37.6	40.3	10.6	60	16
5	35.1	36.8	8.3	60	16
7	32.8	33.9	8.0	60	18
10	29.8	31.0	7.4	62	20
15	21.4	30.0	7.0	65	20
20	15.2	27.6	6.1	68	22
25	7.0	18.5	5.8	70	25
40	2.1	7.2	5.1	75	30

ness properties such tack and peel adhesion rapidly increase, of course on the cost of the cohesion, especially at 70°C.

The amount of silver nanoparticles determines the tack, adhesion, cohesion and electrically conductivity of solvent-borne acrylic PSA formulations. For mentioned properties, silver nanoparticles was selected in an amount ranging from 3 to 40 wt.%. The results obtained for modified acrylic solvent-borne PSA containing silver nanoparticles were shown in Table 2.

The measurement properties values of solvent-borne acrylic PSA characterized for several adhesiveness and cohesiveness performance were illustrated in Figures 2-4.

The addition of silver nanoparticles to solvent-borne acrylic PSA reduces strongly tack and adhesion level.

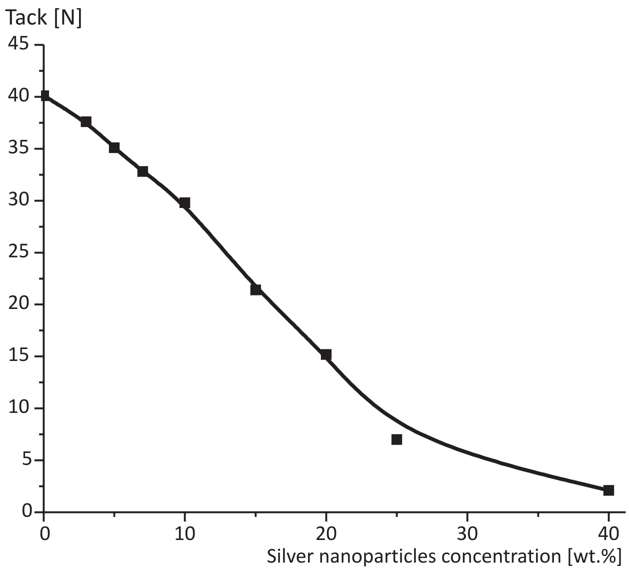


Figure 2. Tack of acrylic PSA as a function of silver nanoparticles content

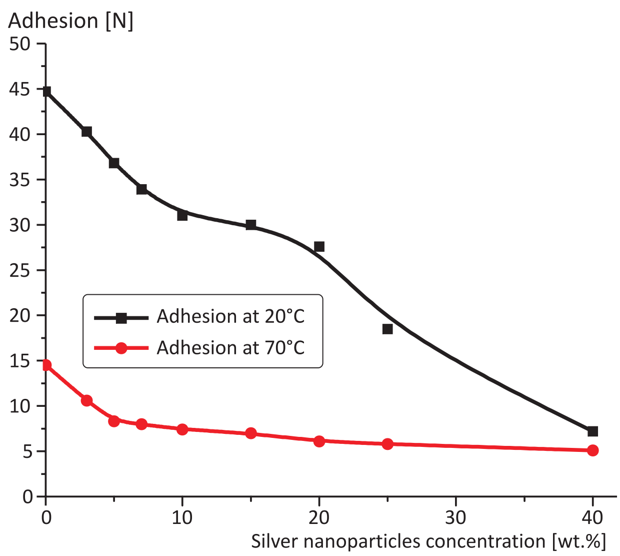


Figure 3. Adhesion of acrylic PSA containing silver nanoparticles

After addition of a small amount of silver nanoparticles, the acrylic PSA begins to crosslink, causing its structure to become compact and its tack and adhesion to increase. This decrease in tack and peel adhesion with increasing silver nanoparticles content due to increased cross-linking degree is opposed by the tendency of higher filler contents to reduction of tack and adhesion level.

Figure 4 is a graph illustrating the relationship between varying silver nanoparticles content and the cohesion, measured at 20°C and 70°C, of acrylic PSA.

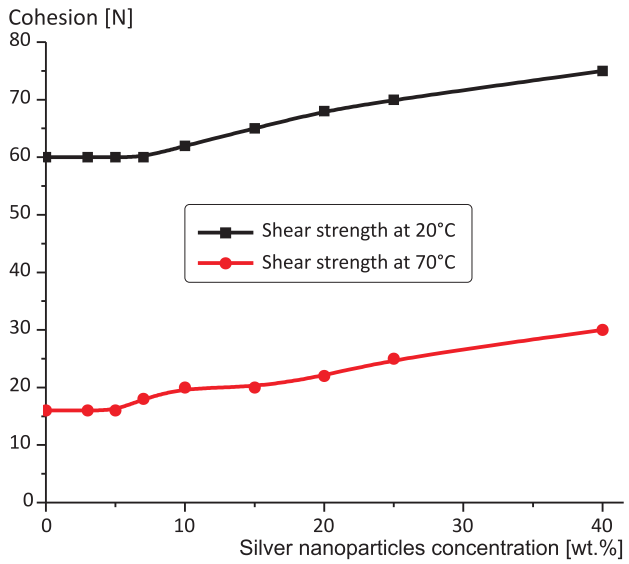


Figure 4. Cohesion of acrylic PSA containing silver nanoparticles

It should be noted that an almost linear relationship exists between the cohesion values experimentally obtained of solvent-borne acrylic PSA and the silver nanoparticles concentration. After addition of silver nanoparticles the reactions between silver and carboxylic groups in acrylic acid are used to link the PSA polymer chains. The higher the silver nanoparticles amount, the higher is the shear strength of acrylic PSA containing silver nanoparticles.

3.1. Electrical conductivity of acrylic PSA containing silver nanoparticles

The addition of electrical conductive silver nanoparticles to the solvent-borne acrylic PSA made it possible to obtain a self-adhesive material with electrically conductivity. The dependence of the electrical conductivity of acrylic PSA containing silver nanoparticles on the filler content is listed in Table 3 and shown in Fig. 5. The reported values represent the average of the three readings. The results show the expected trend of increasing in electrically conductivity with increasing of silver nanoparticles loading.

Table 3. Electrically and optical properties of acrylic PSA containing silver nanoparticles

Silver nanoparticles [wt.%]	Surface resistivity [Ω·cm]	Electrical conductivity [S/cm]	Quality of PSA layer surface
0	10^{11}	10^{-11}	very good
3	10^{11}	10^{-11}	very good
5	10^{11}	10^{-11}	very good
7	10^{11}	10^{-11}	very good
10	10^{9}	10^{-9}	good, acceptable
15	20	0.05	good, acceptable
20	1	1	good, acceptable
25	$9.1 \cdot 10^{-4}$	110	good, acceptable
40	$8 \cdot 10^{-3}$	125	good, acceptable

The electrical conductivity in the case of about 25 wt.% silver nanoparticles shows relatively high and stable level (Fig. 5). The electrical conductivity of the acrylic PSA with 25 wt.% and higher concentration of silver nanoparticles was relatively high. For higher concentration of silver nanoparticles the electrical conductivity values of self-adhesive layers strong increase.

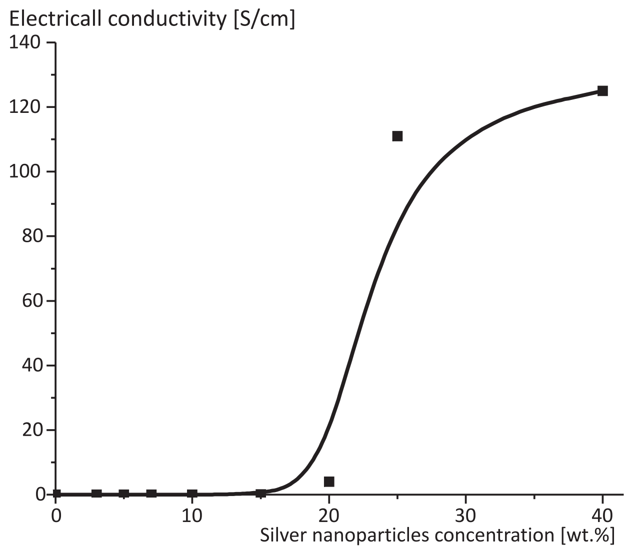


Figure 5. Electrical conductivity of acrylic PSA as a function of silver nanoparticles content

As the silver nanoparticles concentration increased further, the electrical conductivity of the self-adhesive layers increased significantly. The contact points of many sphere particles such improving without any doubt the electrical conductivity of the developed acrylic pressure-sensitive adhesives layers. In fact, no separation of the conductive silver nanoparticles each over in the solvent-borne acrylic PSA is very effective on forming the percolation. The electrically conductive solvent-borne acrylic pressure-sensitive adhesives containing silver nanoparticles remained optically homogeneous (Fig. 6). It is difficult to determine the aspect ratio for the silver nanoparticles since it appears to be somewhat irregular in appearance.

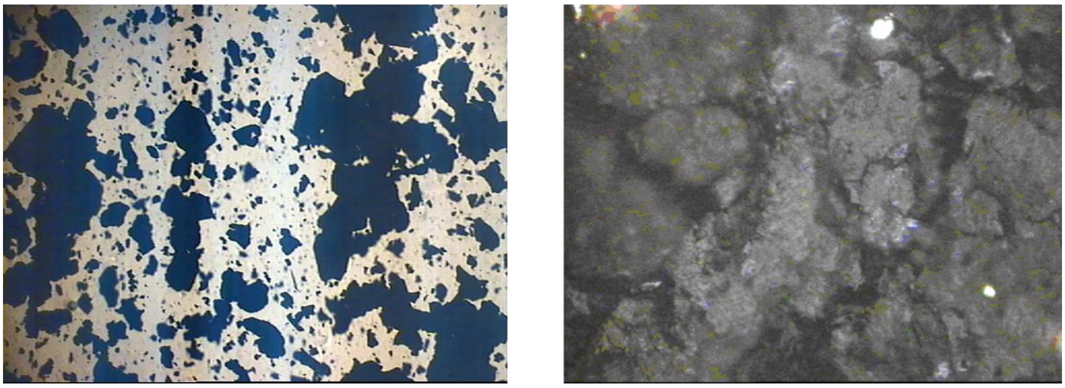
As observed in photos shown in Figure 6, all investigated acrylic PSA modified with different amounts of silver nanopartcles are optically characterized by similar good-looking surfaces.

Figure 7 has demonstrated the structure of the acrylic PSA layers surfaces containing 5 wt.% and 40 wt.% silver nanoparticles performed under optical microscope Nikon Eclipse E600 in 40 blow-up.

The photos, illustrates 20 and 40 wt.% silver nanoparticles, show clearly the contact places of several spheres particles what ameliorate without doubt electrically conductivity of developed acrylic pressure-sensitive adhesives layers. Based on the morphological test, the conducting particles are not perfectly spherical shape and the distribution of silver nanoparticles particles is not perfectly uniform. This

5 wt.% Ag 20 wt.% Ag

Figure 6. Photos of acrylic PSA layers containing different amounts of silver nanoparticles



5 wt.% silver nanoparticles   40 wt.% silver nanoparticles

Figure 7. Acrylics PSA layers containing 5 and 40 wt.% of silver nanoparticles

random distribution of the metal particles shows that it is not a homogeneous medium and a point contact between particle and particle. The silver nanoparticles are buried in the acrylic polymer matrix.

3.2. Stability of solvent-borne acrylic PSA containing silver nanoparticles

The electrically conductive solvent-borne acrylic PSAs containing between 20 and 40 wt.% silver nanoparticles remained optically homogeneous for several hours and were stable for longer than 30 days (Fig. 8). The evaluated viscosities are listed in Table 4. Prior to the coating process the adhesives containing the filler had to be thoroughly mixed. The pressure-sensitive adhesive layers containing silver nanoparticles were silver-coloured.

As it can be seen in Figure 8, the viscosities of solvent-borne acrylic PSAs containing a high contents of silver nanoparticles between 20 and 40 wt.%, according to polymer content, are relatively stable and the resulted modified electrically conductive acrylic PSA can be, after 1 month, uncomplicated coated on adhesive carrier or directly on carrier material to manufacture electrically conductive self-adhesive products. It is very easy to stabilize the acrylic PSAs containing silver nanoparticles. The pot-life of such acrylic adhesives has been longer than a one month. After one month of storage time of the best stabilization has been observed for solvent-borne acrylic PSA, which contained 20 wt.% silver nanoparticles. Using isopropyl alcohol stabilizer can prolong the pot-life of the solvent-borne PSA solutions containing silver nanoparticles, even up to 6 months.

4. CONCLUSIONS

The addition of silver nanoparticles to solvent-borne acrylic PSA reduces tack and adhesion level of self-adhesive layers. The electrically conductive solvent-borne acrylic pressure-sensitive adhesives containing silver nanoparticles remained optically homogeneous and were silver-coloured. The electrical conductivity of the acrylic PSA layers filled with 25 wt.% and higher concentration of silver nanoparticles

Table 4. The pot-life of solvent-borne acrylic PSAs containing silver nanoparticles

Silver nanoparticles	Viscosity [Pa·s] after……..days								
[wt.%]	0	1	2	3	5	10	15	25	30
20	1.2	1.2	1.2	1.2	1.3	1.4	1.6	1.9	2.3
25	1.2	1.2	1.2	1.3	1.5	1.7	1.9	2.2	2.7
30	1.2	1.2	1.2	1.3	1.7	1.9	2.1	2.8	3.6

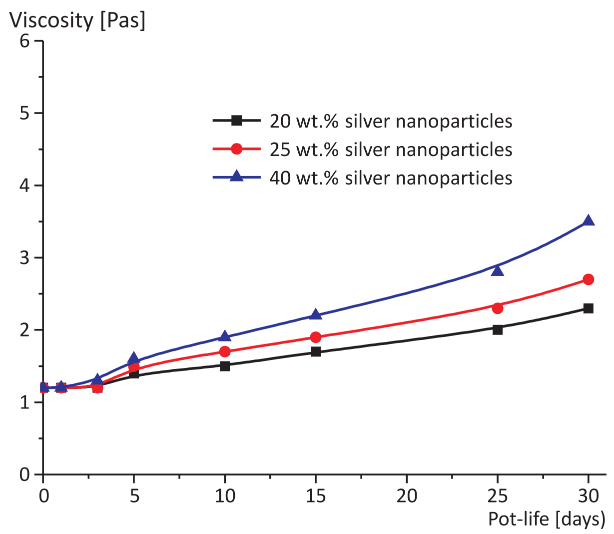


Figure 8. Pot-life of selected solvent-borne acrylic PSAs containing silver nanoparticles

shows relatively high level of 110 S/cm. The percolation threshold was observed at 20 to 25 wt.% fillers resulting in the electrical conductivity from about 1 to 110 S/cm. For higher concentration of silver nanoparticles, the electrical conductivity values of self-adhesive layers greatly increased. Prior to the coating process the adhesives containing the filler had to be thoroughly mixed. It is very easy to stabilize the solvent-borne modified acrylic PSA containing silver nanoparticles. Their pot-life is longer than a one month. Using isopropyl alcohol stabilizer helped to prolong the pot-life of the solvent-borne PSA containing silver nanoparticles even up to 6 months. The novel electrically conductive acrylic pressure-sensitive adhesives containing electrically conductive silver nanoparticles can be used for a manufacturing of wide variety self-adhesive materials with varied electrical properties such as electrically conductive tapes and films with reliable bonds, skin-friendly medical electrodes, antistatic products, self-heating self-adhesive materials, shielding tapes for radiofrequency and electromagnetic insulation, touch screens, computer and automotive electronics, and electromagnetic radiation-absorbing materials.

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