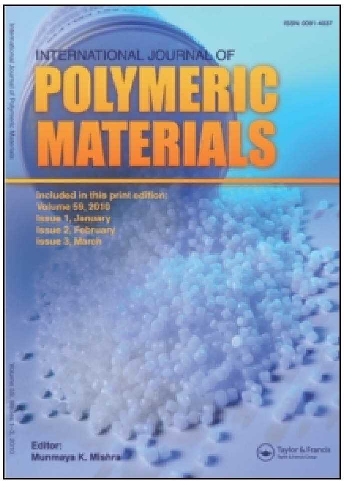


**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Behavior of Pressure-Sensitive Adhesives Filled with Metallized Inorganic Particles

I. Novák[a]; Š. Florián[a]; V. Pollák[a]
[a] Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic

**To cite this Article** Novák, I. , Florián, Š. and Pollák, V.(2007) 'Behavior of Pressure-Sensitive Adhesives Filled with Metallized Inorganic Particles', International Journal of Polymeric Materials, 56: 8, 841 — 849
**To link to this Article: DOI:** 10.1080/00914030701307870
**URL:** http://dx.doi.org/10.1080/00914030701307870

*International Journal of Polymeric Materials*, 56:841–849, 2007

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701307870



# Behavior of Pressure-Sensitive Adhesives Filled with Metallized Inorganic Particles

**I. Novák**
**Š. Florián**
**V. Pollák**
Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic

*The electrically conductive pressure-sensitive composite adhesives based on acrylic polymer and silver-coated inorganic particles have been investigated in this article. The electrical conductivity of the pressure-sensitive adhesives containing silver coated spherical inorganic particles is lower at the same concentration of the filler in comparison with silver coated inorganic fibers, the strength of adhesive joint to aluminum being higher in the case of the pressure-sensitive adhesive containing silver-coated inorganic fibers. After the thermal treatment the strength of adhesive joint to aluminum of electrically conductive pressure sensitive adhesives increases significantly. The suitable concentration proposition of the silver-coated inorganic filler in the pressure-sensitive adhesive requires a compromise solution of the problem taking into account the ultimate adhesive and electrical properties of the investigated pressure-sensitive adhesives composites.*

**Keywords:** adhesives, conductivity, filler, polyacrylate

## INTRODUCTION

The development of pressure-sensitive, electrically conductive self-adhesive coatings is necessary for special technological processes in many branches of the industry [1–7]. The electrically conductive pressure-sensitive adhesives (PSAs) are widely used in light-current

Received 27 December 2006; in final form 31 December 2006.
The authors are grateful to the Slovak grant agency VEGA (Grant No. 2/7103/27) for the financial support of this research.
Address correspondence to I. Novák, Polymer Institute of the Slovak Academy of Sciences, Department of Composite Thermoplastics, Dubravska cesta 9, 842 36, Bratislava, Slovak Republic. E-mail: upolnovi@savba.sk

electro-technical engineering. The polymer matrix of this type of PSAs contains dispersed (generally submicron) metallic, metal-coated, or carbonaceous electrically conductive particles [2–9]. The electrically conductive PSAs can be also produced from inherently electrically conductive polymer materials. At the process of the construction of the modern electrical and electronic components, the isotropic electrically conductive PSAs that display equal electrical conductivity in all direction are usually used [10–20].

The preparation of the adequate electrically conductive PSAs is rather complicated because of requirements contradictory to their properties [1,7,8,12]. The concentration of electrically conductive filler in PSAs needs to be reasonably high for obtaining appropriate electrical conductivity, but on the other hand, increase of the filler concentration above a certain level diminishes the cohesive and adhesive properties of these adhesives.

The electrically conductive PSAs are used for preparation of the electrically conductive tapes consisting of polymer film (e.g., polyester, biaxially oriented modified isotactic polypropylene) and layer of the adhesive. The adhesives are usually formulated on the base of polyacrylate, elastomers, or amorphous polyolefins, which must exhibit the required adhesive characteristics combined with sufficient electrical properties.

The raw materials for the preparation of the electrically conductive PSAs need to be physically and chemically stable with respect to moisture and voltage. The PSAs on the base of tacky polyacrylate are frequently used for statically stressed adhesive joints and they are appropriate for cyclic load perpendicular to a layer of PSA. It is very important to determine the optimum concentration of tackifier in electrically conductive PSAs composite from the point of view of the harmonization of adhesive, electrical, and mechanical properties.

This contribution deals with the adhesive and electrical properties of isotropic electrically conductive PSAs on the base of polyacrylates filled with silver-coated electrically conductive basalt particles or wollastonite fibers.



## EXPERIMENTAL

### Adhesive

The following PSA was used: statistical (styrene-2-ethylhexyl acrylate) copolymer ($M_w = 2.7 \times 10^4$) containing 14 wt% of styrene (Synpo, Czech Republic).

## Aluminum

The aluminum alloy was MgAlSi0.5 [OKD, Slovakia] with a composition: 98.45 wt% of Al, 0.7 wt% of Mg, 0.5 wt% of Si, 0.2 wt% of Fe, and 0.15 wt% of Mn.

## Fillers

The wollastonite fibers (mineral fibers based on calcium silicate) Nyglos 12 (Nyco, Belgium) with the length of the fibers = 156 μm, diameter of fibers = 12 μm, and aspect ratio = 13; basalt particles ($d < 40$ μm) having an irregular spherical shape (Zelba, Slovak Republic).

## Electro-Less Plating of the Filler

The silver-coated fillers were prepared using a method of electro-less plating [8,12]. The following solutions were prepared:

Solution **A** consists of 300 g of silver nitrate in 1000 ml of distilled water. After the dissolution of the silver nitrate, the 10% water solution of the ammonia is added under stirring up to dissolution of the present sediment.

Solution **B** (reduction solution) consists of 245 g sodium-potassium tartrate dissolved in 940 ml distilled water. After dissolution of the sodium-potassium tartrate, the 40% formaldehyde is added up to creation of the visible turbidity (approximately 30 ml).

Solution **C** consists of 100 ml of solution A dissolved in 900 ml of distilled water.

Solution **D** consists of 200 ml of solution B dissolved in 800 ml of distilled water.

Final solution **E** for the silver-plating of the filler is prepared closely before use by mixing of 100 ml of solution C and 20 ml of solution D.

The inorganic fillers were plated in solution E at ambient temperature during 20 min, then washed thoroughly in distilled water and dried at 60°C.

## Preparation of the Composites

The mixing process was carried out in the polymeric melt by mixing of (styrene-2-ethylhexyl acrylate) copolymer with respective electrically conductive inorganic filler using laboratory kneading machine (Koba, Slovak Republic). The mixing temperature was 110°C, a speed of mixing 20 rpm, and a mixing time of 20 min using silicone oil as a heating medium.

## Measurement of the Strength of Adhesive Joint

The surface of aluminum was cleaned with acetone and subsequently was dried with n-propanol. Two 40 mm aluminum discs were coated with uniform layer of the PSA with the thickness 0.2 mm and annealed at 100°C for 20 min. The butt joints were prepared by pressing together the aluminum discs by applying a 0.3 MPa pressure for 120 s. The strength of the adhesive joints has been tested by universal Testing Machine Instron 4301 containing respective computer software. The rate of motion of dynamometer crosshead was 10 mm·min$^{-1}$.

## Measurement of the Electrical Resistance

The volume electrical resistance of electrically conductive adhesives was measured according to ASTM D-257. The diameter of the sample was 50 mm and its thickness 1.0 mm. A three-electrode electrometer apparatus [8,20] with stabilized power supply unit AT 3067 (Czech Republic) or high-voltage power supply unit Statron 4205 (Germany), and a picoammeter Tesla BM 545 (Czech Republic) was used for the DC-measurement of the resistance. The voltage level varied in the range of 0.1 to 500 V. The samples were measured at the room temperature and 50% humidity.



# RESULTS AND DISCUSSION

Figure 1 represents volume electrical resistance of the electrically conductive PSAs on the base of polyacrylate filled with silver-coated basalt particles or wollastonite fibers.

The plot "a" in Figure 1 gives the concentration dependence of the volume electrical resistance of PSA composites for plated basalt particles. It appears that values of the electrical resistance drop very slowly up to the concentration of about 23 vol%. Increasing the plated basalt particle concentration above this level, the resistance shows sharp decrease. Although the value of volume electrical resistance of non-filled polymer is 13.2 it decreases to 4.2 at 36 vol% of plated basalts particles owing to percolation concentration of conductive filler and continues to decrease to 1.4 at 41 vol% of this filler in adhesive. If the plated basalt particles are replaced by plated wollastonite fibers exhibiting smaller dimensions (the size of irregular spherical particles of basalt is 40 μm, whereas the average diameter of wollastonite fibers is about 12 μm), the percolation concentration can be reached at considerably lower concentration of plated wollastonite fibers (Figure 1, plot b), when compared with plated basalt particles (Figure 1, plot a). If the content of silver-coated wollastonite in adhesive continued

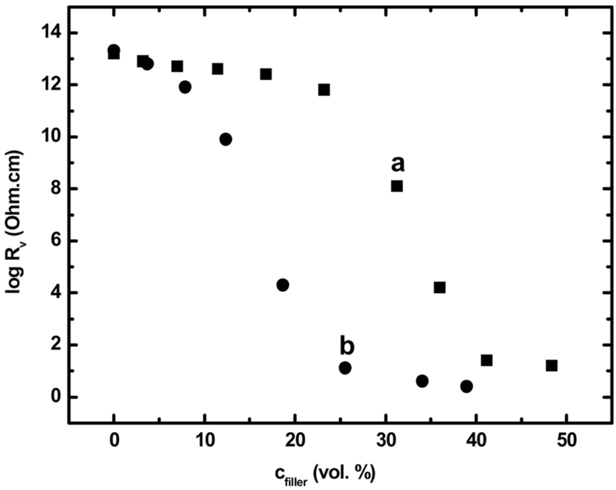


**FIGURE 1** Variation of the electrical resistance of pressure-sensitive adhesive with content of the plated filler: basalt particles (a), wollastonite fibers (b).



to increase, the value of volume electrical resistance decreased to 0.4 (for 39 vol% of the filler in adhesive).

Figure 2 shows the strength of adhesive joint between PSA composite and aluminum for varying content of conductive filler in the system adhesive/plated basalt particles, plot a, and adhesive/plated wollastonite fibers, plot b.

According to Figure 2, plot b, the strength of adhesive joint drops from the value of 0.18 MPa (unmodified PSA) to 0.01 MPa (45 vol% filling) for silver-plated basalt particles. At 26 vol% of filling, the value of the strength of adhesive joint shows only about 50% of original strength, the 39 vol% filling by silver-plated basalt particles causes the reduction of the joint strength to 0.04 MPa. The results are different in the case of the silver-coated wollastonite fibers. Because of its fibrilar character, this material establishes electrical contact at the lower filler concentrations in comparison with plated basalt particles. The plot a in Figure 2 shows that the increased concentration of the plated wollastonite fibers does not produce such considerable change in strength of adhesive joint as observed in the preceding case. The strength of adhesive joint is 0.15 MPa for 23 vol% of wollastonite fibers, whereas the original strength for unfilled adhesive system is 0.18 MPa. The silver-plated basalt particles exhibited the strength of the adhesive joint to aluminum 0.08 MPa and electrical resistance in logarithmic form 8.1, whereas the plated fibers of wollastonite

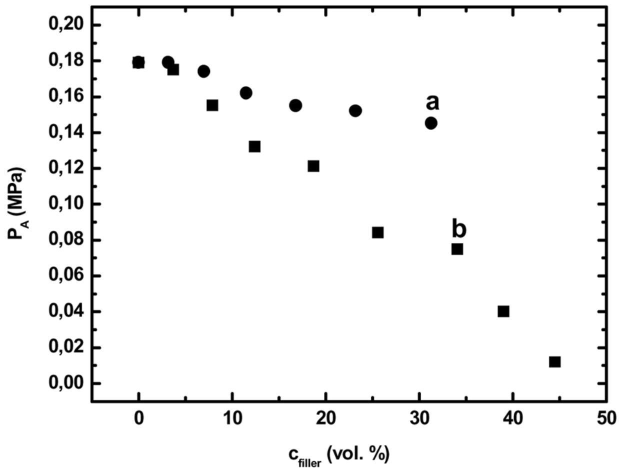


**FIGURE 2** Variation of the strength of adhesive joint of pressure-sensitive adhesive to aluminum with content of the plated filler: wollastonite fibers (a), basalt particles (b).



exhibited the strength of adhesive joint 0.15 MPa and volume electrical resistance 0.8 ohm·cm. Thus, the PSAs displayed higher strength of adhesive joint to aluminum and higher electrical conductivity at a given concentration of plated wollastonite fibers when compared with adhesives containing plated basalt particles.

Figure 3 represents the strength of adhesive joint versus the logarithm of volume electrical resistance for the joints using PSA adhesive filled by silver-coated wollastonite fibers (plot a) and basalt particles (plot b). According to Figure 3, the strength of adhesive joints is substantially higher in the case of the fibers filled adhesive. However, the difference between the strength of adhesive joint is much more pronounced in the region of high filling. The dependence of the adhesive joint strength versus the logarithm of volume electrical resistance presented in Figure 3 for the adhesive filled with silver-plated wollastonite (plot a) displays only slight slope. The strength of adhesive joint drops from original value of 0.18 MPa valid for unfilled system to 0.15 MP avalid for PSA containing 23 vol% of silver-plated wollastonite fibers. It can be seen that the strength of adhesive joint dropped only by 5%, whereas the conductivity of the joints is adequately high (log $R_v = 0.8$), (Figure 1, plot b, Figure 2, plot a). Therefore, it can be stated that the fibrous plated wollastonite is more suitable for preparation of electrically conductive adhesive than plated basalt particles.

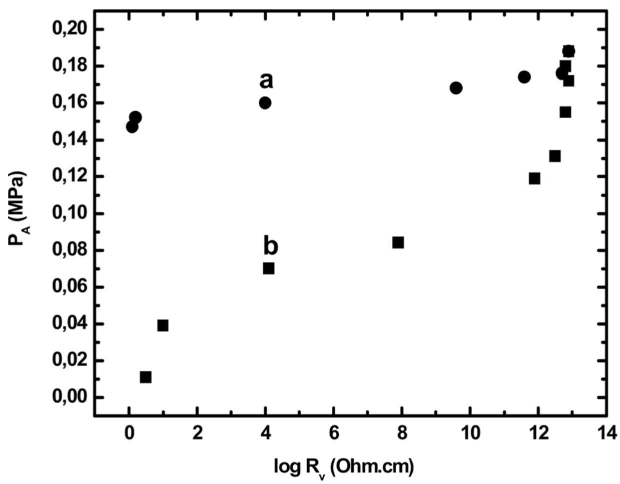


**FIGURE 3** Variation of the strength of adhesive joint of pressure-sensitive adhesive to aluminum with electrical resistance: wollastonite fibers (a), basalt particles (b).



Figure 4 represents the dependence of the strength of adhesive joint versus plated basalt filler content for annealed and non-annealed PSA aluminum-aluminum joints.

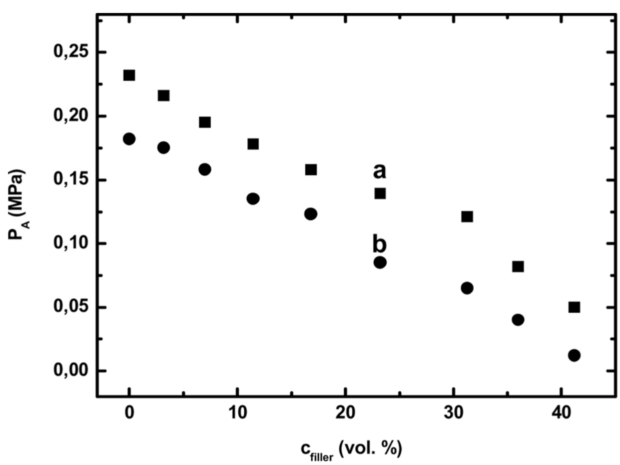


**FIGURE 4** Variation of the strength of adhesive joint of pressure-sensitive adhesive filled with plated basalt particles to aluminum with content of the filler: non-annealed sample (a), sample annealed 48 h at 100°C (b).

The annealing of the sample of the PSA filled with silver-coated particles leads to the increase of the strength of adhesive joint from 0.18 to 0.23 MPa for unfilled adhesive, from 0.09 to 0.14 MPa for 23.2 vol% of the filler in adhesive, and from 0.01 to 0.05 MPa for 45 vol% of the filler in adhesive.

The annealing under given conditions (48 h, 100°C) probably induces the degradation of polyacrylate with the result of the better wetting of the aluminum surfaces. Consequently, the strength of adhesive joint to aluminum appreciably increases. This increase of the strength of adhesive joint could be substantially important for the practical use of plated basalt particles.

## CONCLUSION

The adhesive and electrical properties of PSAs formulated on the base of polyacrylate and plated inorganic particles are dependent on the type and shape of particles of the used filler. In the case of silver-coated basalt particles, the percolation concentration was reached at substantially higher concentration of the plated filler in comparison with the plated wollastonite fibers. The plated wollastonite fibers appear to be more appropriate for obtaining strong adhesive joints. A certain solution of the problem of the lower adhesive strength of the plated basalt containing adhesives consists of the annealing of the adhesive joint. After the thermal pre-treatment, the strength of adhesive joint significantly increases even at the higher concentration of the filler in the PSA composite. The preparation of the pressure-sensitive adhesives containing silver-coated inorganic particles requires compromise solution of the problem with regard to the selection of the adhesive and the electrical parameters of the investigated system.



## REFERENCES

[1] Novák, I. and Florián, S., *J. Mater. Sci. Lett.* **22**, 1237 (2003).
[2] Luyt, A. S., Molefi, J. A., and Krump, H, *Polym. Derad. Stab.* **91**, 1629 (2006).
[3] Florián, S. and Novák, I., *Angew. Makromol. Chem.* **239**, 55 (1996).
[4] Sun, J., Gerberich, W. W., and Francis, L. F., *J. Pol. Sci., Part B, Polym. Phys.* **41**, 1744 (2003).
[5] Boudenne, A., Ibos, L., Fois, M., Gehin, E., and Majeste, J. C., *J. Polym. Sci., Part B, Polym. Phys.* **42**, 722 (2004).
[6] Foulger, S. H., *J. Appl. Polym. Sci.* **72**, 1573 (1999).
[7] Novák, I., Krupa, I., and Chodák, I., *Synth. Met.* **131**, 93 (2002).
[8] Novák, I., Krupa, I., and Chodák, I., *Synth. Met.* **144**, 13 (2004).
[9] Figovsky, O. L., Sklyarsky, L. S., and Sklyarsky, O. N., *J. Adhes. Sci. Technol.* **14**, 915 (2000).

[10] Savolainen, P. and Kivilahti, J., *J. Adhesion* **49**, 187 (1995).
[11] Sancaktar, E. and Dilsiz, N., *J. Adhesion Sci.* **13**, 679 (1999).
[12] Novák, I., Krupa, I., and Chodák, I., *Eur. Polym. J.* **39**, 585 (2003).
[13] Kim, H. K. and Shi, F. G., *Microelectr. J.* **32**, 315 (2001).
[14] Lu, D., Tong, Q. K., and Wong, C. P., *IEEE Transactions on Electronics Packaging Manufacturing* **22**, 223 (1999).
[15] Chodák, I. and Krupa, I., *J. Mat. Sci. Lett.* **18**, 1457 (1999).
[16] Ma, C. C. M., Chen, Y. J., and Kuan, H. C., *J. Appl. Polym. Sci.* **100**, 508 (2006).
[17] Boudenne, A., Ibos, L., Fois, M., Majeste, J. C., and Gehon, E., *Composites, Part A, Appl. Sci. Manufact.* **36**, 1545 (2005).
[18] Dong, Q. Q., Zheng, Q., and Zhang, M. Q., *J. Mater. Sci.* **41**, 3175 (2006).
[19] Lebowka, N. I., Lisunova, M., Mamunya, Y. P., and Vygornitskii, N., *J. Phys. D, Appl. Phys.* **39**, 2264 (2006).
[20] Novák, I., Krupa, I., and Janigová, I., *Carbon* **43**, 841 (2005).