Key Engineering Materials

Volume I

Current State of the Art on Novel Materials

Editors
Devrim Balköse, PhD
Daniel Horak, PhD
Ladislav Šoltés, PhD

Apple Academic Press

CRC Press
Taylor & Francis Group

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Apple Academic Press

TORONTO NEW JERSEY

Apple Academic Press Inc.
3333 Mistwell Crescent
Oakville, ON L6L 0A2
Canada

Apple Academic Press Inc.
9 Spinnaker Way
Waretown, NJ 08758
USA

Printed in the United States of America on acid-free paper

International Standard Book Number-13: 978-1-926895-73-4 (Hardcover)

Library of Congress Control Number: 2013956108

Library and Archives Canada Cataloguing in Publication

Key engineering materials.

Includes bibliographical references and index.
Contents: v. 1. Current state of the art on novel materials/edited by Devrim Balköse, PhD, Daniel Horak, PhD, and Ladislav Šoltés, DSc; A. K. Haghi, PhD, and G. E. Zaikov, DSc, reviewers and advisory board members -- v. 2. Interdisciplinary concepts and research/edited by François Kajzar, PhD, Eli M. Pearce, PhD, Nikolai A. Turovskij, PhD, and Omari Vasilii Mukbaniani, DSc; A. K. Haghi, PhD, and Gennady E. Zaikov, DSc, reviewers and advisory board members.
ISBN 978-1-926895-73-4 (v. 1 : bound)

1. Materials. I. Balköse, Devrim, editor of compilation II. Horák, D. (Daniel), editor of compilation III. Šoltés, Ladislav, editor of compilation IV. Title: Current state of the art on novel materials. V. Title: Interdisciplinary concepts and research.

TA403.K49 2014 620.1'1 C2013-908007-4

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CHAPTER 10

NEW TYPES OF ETHYLENE COPOLYMERS ON THE BASE NANOCOMPOSITE

IGOR NOVÁK, PETER JURKOVIČ, JÁN MATYAŠOVSKÝ, and LADISLAV ŠOLTÉS

CONTENTS

10.1 INTRODUCTION

This chapter deals with adhesive and mechanical properties study of nanocomposites based on ethylene-acrylic acid copolymer during aluminum bonding. The main objective was to describe the changes of copolymer properties during increasing of the nanofiller's concentration. Based on executed experiments it was found out, that the properties of tested nanocomposite system were mostly improved depending on the contents of the nanofiller in the system. The optimum concentration of nanofiller Aerosil 130 SLP in the composite was 2.5 wt% for cohesive mechanical properties of the system and 3.5 wt% for adhesive ones. Thermal properties of the composite system showed their maximum within concentration of 4.5 wt% of nanofiller.

When compared with other types of composites, thermoplastics have some advantages.

- They are solvent-free and non-toxic (in most cases).
- They are characterized by short time of creation of adhesive bond respectively foil.
- They are applicable at low temperatures.
- They ensures high adhesion to different material and high impact strength of the joint.
- They ensure suitable initial strength of adhesive joints.
- They have good storage stability.
- They are proper for gluing automation and increasing labor productivity
- No undesirable moisture is brought into the materials—it means that there is not necessary the long-term storage of products in conditioned environment.

Nowadays, adhesives based on EAA (ethylene–acrylic acid) copolymers, EVA (ethylene–vinyl acetate) copolymers, thermoplastic polymers, polyamide, polyesters, polyethylene, and cellulose [1-6] belong to most often used composites. By addition of a proper type of filler, mentioned properties can be even improved. The aim of this contribution is to evaluate the influence of nanofiller on the properties of EAA copolymer.

10.2 EXPERIMENTAL PART

As a polymer, EAA copolymer MICHEM Adhesive 20 EAA, with the ratio of 20% wt. of acrylic acid and the ratio of 80% wt. of ethylene, was used. Characteristic properties of the product are:

- Appearance: slight turbidity, almost transparent polymer,
- Density: 1.3 g/cm^3,
- Melt flow: 1.8 g/10min,
- Content of volatiles: less than 0.1 wt.%.

Aerosil 130 SLP (Degussa comp.) was used as filler into nanocomposite system. Aerosil is a flame-patterned silica oxide with an average particle size from 40 to 50 nm. Figure 1 shows the microscopic image of used filler. As we can see, the structure of the filler is spherical with a minimal difference in particles size and non-porous solid surface.

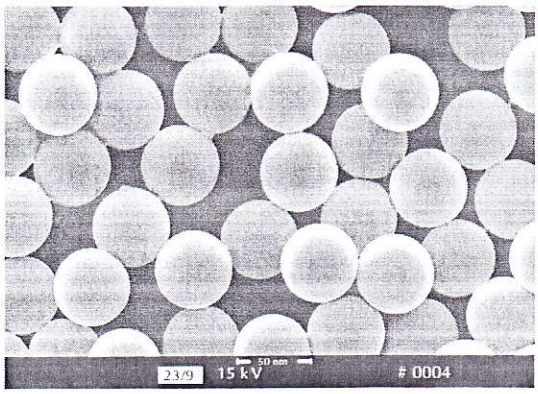

FIGURE 1 The detail of Aerosil 130 SLP particles.

For preparation of nanocomposite system, EAA copolymer was used as the base for copolymer matrix which was blended with the filler in concentrations 0, 0.5, 1, 1.5, 2.5, 3.5, and 4.5% wt. To mix the mixture, we used Plastograf Brabender PLE 331 heated by silicone oil in fully filled tank W-50-hr (volume 50 cm^3). The temperature at mixing of nanocomposite was adjusted to 180°C by a thermostat containing tempered silicone medium. Mixing was at 35 rpm^{-1} for 10 min at predetermined temperature. Considering the properties of individual components, it was preferable to use a triangular blade.

At measurement of adhesive characteristics, the aluminum sheet with thickness of 2 mm and chemical composition listed in Table 1 was used.

TABLE 1 Chemical composition of adherends

Elements	Al	Cu	Fe	Mg	Mn	Ni	Si	Zn
Content (wt. %)	99.5	0.0025	0.32	0.002	0.0035	0.013	0.12	0.007

To measure the peeling strength of adhesive joint, the aluminum foil AlMgSi 0.5 with thickness of 0.1 mm were used.

Before gluing, the surface of adherents was grinded with 120 grit sandpaper and then scratches were aligned with 1000 grit sandpaper. Afterwards, the surface was cleaned of grease and other dirtiness with a mixture of benzene and toluene (volume ratio 1:1). To ensure a constant spacing between bonded adherents and an equal thickness of adhesive, two distant wires with diameter ϕ 0.15 mm were placed parallel on the bottom board.

The surface of aluminum foil used in the peeling test was only ungreased with a mixture of benzene and toluene. To measure cohesive characteristics, it was necessary to make test blades according to Figure2.

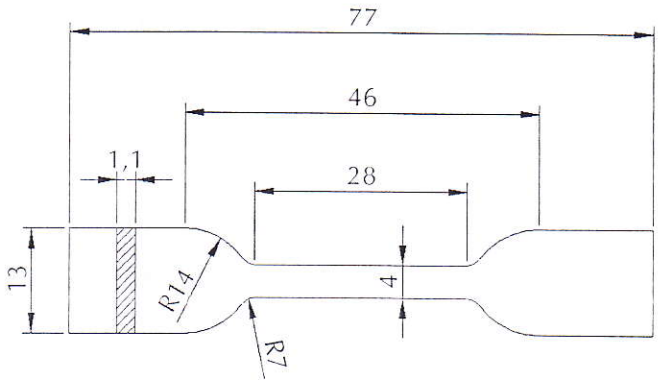

FIGURE 2 Specimen for testing of tensile strength.

To make them, first boards from filled and unfilled systems (dimensions of 74 × 100 × 1.1) were prepared in a shape in hydraulic press at 180°C, pressure 250 kPa, for 5 min. After cooling of them in a mechanical press, test blades were scissored.

For preparing the samples for testing of adhesive properties (Figure 3), thin layer of hot-melt adhesive was inserted between two cleaned and ungreased aluminum boards with distant wires ϕ 0.15 mm. Lap joint was foil-wrapped into teflon foil and the whole sample was fixed with aluminum foil and put between press plates tempered at 180°C. At pressure of 100 kPa during 5 min, lap joint was formed. The specimens for peeling test were made similarly.

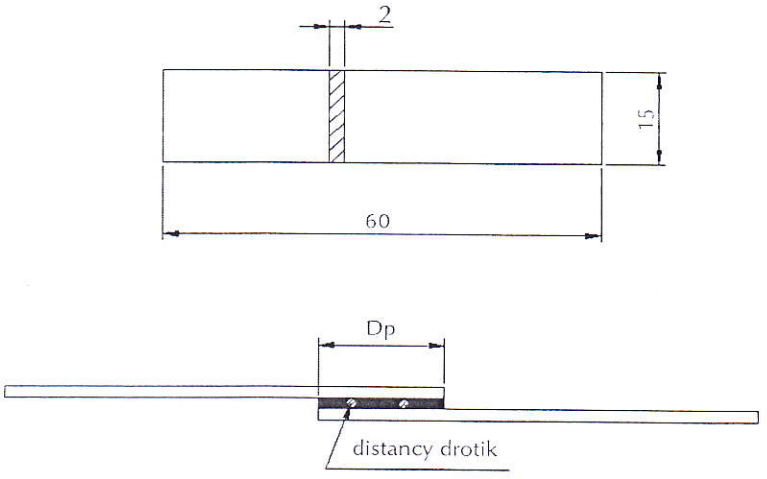

FIGURE 3 Lap adhesive joint.

Methods of testing included mechanical tests (measurement of cohesive properties and hardness), adhesive tests (measurement of shear strength of adhesive joint at loading by tension [2], measurement of strength of adhesive joint at peeling [3], measurement of surface properties, thermo gravimetric analysis, and measurement of thermal properties.

Measurement of cohesive characteristics included the loading the test blade by tensile (Figure 1) at rate of separation of the jaws 50 mm/min with machine Instron 4301 (Instron, England), when following characteristics were evaluated—maximal tensile strength (MPa), maximal elongation (%), elongation at rupture (%), tensile strength at rupture (MPa), Young module of elasticity (MPa), yield strength (MPa), and elongation at yield.

Measurement of hardness in ShD was done according to ASTM D 2122-2. Equipment D Scale Durometer PTC 307—L designed for plastics and react-plastics was used.

To measure adhesive characteristics, the test machine Instron 4301 was used (rate of separation of the jaws 50 mm/min). Following characteristics were evaluated:

- Shear strength (MPa)
- Relative elongation (%)
- Young module of elasticity (MPa)
- Energy of destruction of adhesive joint (J)

At peel test, the tested specimen was fixed in testing machine Instron 4301. Board A1 was fixed in the low jaw and aluminum foil was fixed in the upper movable jaw. Rate of separation was slower, only 10 mm/min. The values evaluated were:

- Strength of the joint at maximal loading (MPa)
- Average peel power (N)
- Average tear tension (N/mm)

Besides, also thermographic analysis was done with a thermogravimeter TG-1 (Perkin Elmer, USA).

10.4 DISCUSSION AND RESULTS

The Figure 4 presents the dependence of maximal tensile strength (R_{max}) and tensile strength at breaking (R_r) on the content of filler in composite adhesive. From measured results follow, that with increasing content of nanoparticles of filler in EAA, the maximal tensile strength of composite is non-linearly increased. It can be assumed, that further filling will increase the value of maximal tensile strength but only for certain concentration. At this concentration, EAA composite will be saturated with Aerosil 130 SLP, what causes insufficient wetting of surface of filler particles and following lowering of max. tensile strength.

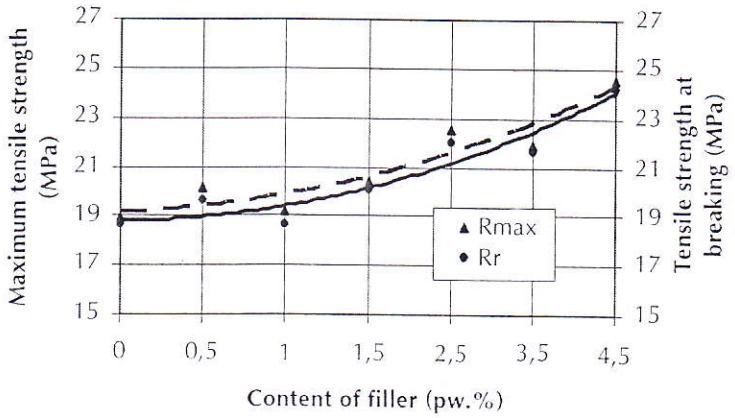

FIGURE 4 Dependence of max. tensile strength (R_{max}) and tensile strength at breaking (R_r) on the content of filler.

The dependence of adhesive shear strength of joint on the content of filler is on the Figure 5. Considering the high specific surface of nanoparticle filler (130 m^2/g), intense change of investigated parameter occurs already at low concentrations of filler. Increased dispersion of measured values can be justified by the possible presence of nonhomogeneous in the composite system, as well as the deteriorative wetting of the aluminum substrate in the growth of filler content. Substantially is worsened the spreading of co-polymer melt adhesive on the glued surface due to an increase melt viscosity of hot melt glue, which deteriorates the surface wetting.

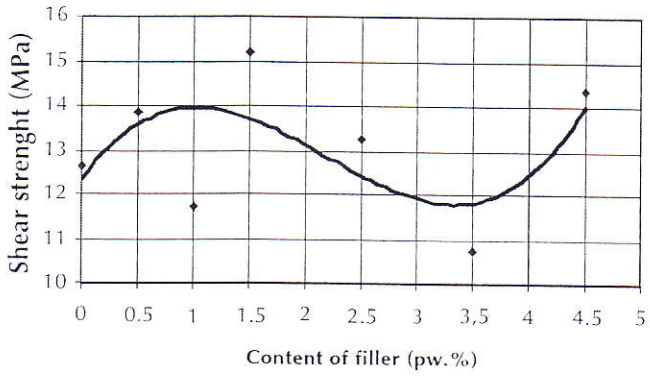

FIGURE 5 Dependence of adhesion joint shear strength on the filler content.

Character of dependence of average peeling stress is parabolic with the maximum at the content of filler 3.5 wt% (Figure 6). Also in this case, measured values show higher variance, similarly as at measurement of adhesive shear strength of joint.

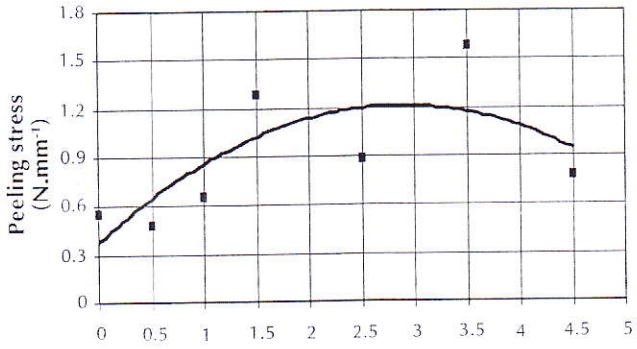

FIGURE 6 Dependence of peeling stress on adhesive concentration.

Thermo gravimetric analysis confirmed, that temperature of 10% weight loss and temperature of sudden weight loss (Figure 7) had after initial decrease increasing tendency. With the increase of filler particles, the temperature of loss 10% weight is increasing from 360 to 385°C, which represents a rise up to 8%. The reason is higher absorption of heat with Aerosil 130 SLP. Temperatures of sudden loss reach lower values (342 up to 374°C) in comparison with the temperature of loss 10% weight.

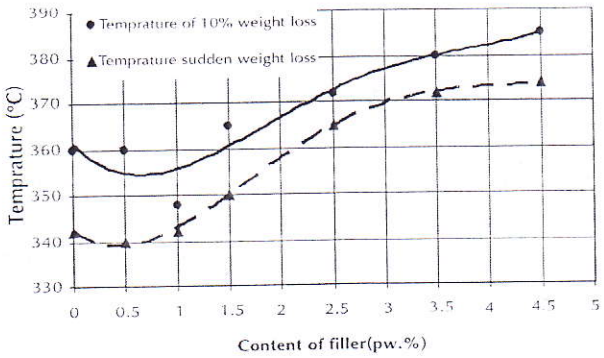

FIGURE 7 The dependence of temperature of 10% weight loss and temperature of sudden weight loss on the content of Aerosil 130 SLP.

10.4 CONCLUSION

On the base of realized experiments it can be concluded, that nanoparticle filler Aerosil 130 SLP influences individual properties of filled EAA system differently. The filler has positive impact to improve the cohesion and adhesion strength, heat resistance, peeling tension, and surface properties of the system. On the other hand, reduces the relative extension, factors of heat and thermal conductivity, and specific volume heat

capacity. The cohesive mechanical parameters of the system can be stated as an optimal concentration of nanofiller Aerosil 130 SLP 2.5 wt%, the adhesion properties of 3.5 wt%. Nanoparticles composite systems showed the highest heat resistance in filler concentration from 3.5 to 4.5 wt%. For practical application of filled EAA nanocomposite systems is therefore necessary to know how to use, environment, application temperature and method of stress, and accordingly select the optimal concentration nanofiller.

KEYWORDS

- Composite
- EAA copolymers,
- Hot-melt adhesives
- Nanofillers

ACKNOWLEDGMENT

This contribution is the result of the project implementation Research of the Application Potential of Renewable and Recycled Materials and Information Technologies in the Rubber Industry" (project code ITMS: 26220220173) supported by the Research and Development Operational Program funded by the ERDF.

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