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Complete List of Authors:	Wang, Yuan; University of exeter, Department of Engineering, Mathematics and Physical Sciences Ghita, Oana; University of exeter, Department of Engineering, Mathematics and Physical Sciences Kavanagh, Dave; Bell Plastics Limited, 450 Blandford Road Chandler, Duncan; Bell Plastics Limited, 450 Blandford Road
Keywords:	interface adhesion, polyamide 6 (PA6), nitrile rubber (NBR), silane modified nano-ZnO

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Review

A study of interface adhesion between polyamide 6 (PA6) and nitrile rubber (NBR)

Yuan Wang^{1*}, Oana Ghita¹, Dave Kavanagh², Duncan Chandler²

¹ University of Exeter, Department of Engineering, Mathematics and Physical Sciences, North Park Road, EX4 4QF, UK

² Bell Plastic Limited, 450 Blandford Road, Poole, BH16 5BN, UK

*corresponding author: y.wang@exeter.ac.uk

Abstract

The mechanism of interface bonding of a selected nitrile rubber (NBR) compound vulcanized on polyamide 6 (PA6) was studied using Transmission Electron Microscopy (TEM). Two types of interfaces, primary and secondary interface were identified. The interface bonding was formed through mechanical clamping and enhanced by hydrogen bonding formation between PA6 and silane coupling agent in NBR compound.

Keywords: interface adhesion, polyamide 6 (PA6), nitrile rubber (NBR), silane modified nano-ZnO

1. Introduction

Zinc oxide (ZnO) is one of the basic additives in rubber compounds. The main function of ZnO is activator of sulphur crosslinking reaction [1]. Nano-ZnO is a more efficient activator compared with conventional micro-ZnO reducing the vulcanization time of sulphur cured rubber, due to increased surface area [2], [3]. Before blending nano-ZnO into rubber, surface modification of nano-ZnO is usually applied to enhance the interfacial interaction between nanoparticles and rubber matrix, and therefore leading to better dispersion of the nanoparticles [4],[5],[6]. In our study, the selected nitrile rubber (NBR) compound which contained silane modified nano-ZnO was cured on a polyamide 6 (PA6) substrate. Severe interface adhesion was found between the two surfaces. This study investigated the mechanism of interface bonding by Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray analysis (EDX). A mechanism is proposed to interpret the bonding between PA6 and NBR rubber compound.

2. Experiment

2.1 Sample preparation

PA6 (Tarnamid®T-30, Azoty Tarnow™, Poland) substrate with dimension of 80×10×4 mm was prepared by injection moulding. The selected NBR compound with 2mm thickness was supplied by Caterpillar Inc. The NBR compound was vulcanized on top of PA6 substrate in a steel mould, which was closed to keep the two materials in good contact but not further pressure was applied. The vulcanization was performed in oven (Genlab Ltd., UK) at 150 °C for 2 hours. NBR compound was fully vulcanized after the heat treatment, and it was entirely bonded to PA6.

2.2 Characterization

TEM specimens were prepared by trimming samples prepared in 2.1 with razor blade to form blocks of approximately 2×2×2 mm. These blocks were further trimmed to the shape of a pyramid with the tip faced off to an area of approximately 0.3×0.3 mm. Then the thin TEM samples were prepared on microtome (Ultracut, Reichert-Jung, USA) from these blocks. The sectioning was performed along the NBR/PA6 interface with a diamond knife. The TEM specimens have an approximately 50µm thickness. The specimens were placed on copper grids. TEM bright field

1 observation, EDX spectrum, EDX mapping and EDX line scan were carried out on JEM 2100
2 (JEOL, Japan) with EDX probe (X-MAX, Oxford instrument, UK), under 200 kV acceleration
3 voltage.
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7 **3. Result**

8 3.1 TEM image and EDX mapping of selected NBR compound

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10 Fig.1 is a TEM bright field image of selected NBR compound, and EDX maps of Si, O and Zn from
11 silane modified nano-ZnO. The maps were taken from identical TEM imaging area. Elemental maps
12 have shown that these three elements accumulated in the same region. As marked by dashed cycles,
13 silane modified nano-ZnO were dispersed in the NBR compound in the form of small clusters
14 which were composed of several agglomerated particles with size of tenth nm diameters. Large
15 particles with diameter above 100nm, presented in the imaging area, were other fillers in the
16 selected NBR compound.
17
18
19

20 3.2 NBR compound/PA6 interface analysis

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22 Fig. 2 illustrates the low magnification TEM image of NBR compound/PA6 interface boundaries in
23 cross section. PA6 substrate was presented on top right of the image and NBR compound was
24 presented on the bottom left of the image. Two types of NBR compound/PA6 interface boundaries
25 were observed: (1) a primary interface boundaries which were directly developed along the contact
26 surface of PA6 substrate and rubber (marked with dashed yellow lines); (2) a secondary interface
27 boundaries which were formed along edges of the micro-cracks, presented inside the rubber
28 (marked with dashed red lines). The width of micro-cracks was approximately 100 μ m.
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30

31 The high magnification TEM image of primary interface (Fig. 3) has shown that the interface was
32 presented as a dark band along the contact surface of NBR compound and PA6 substrate. In the
33 imaging area, the thickness of interface was in a range of 100-400nm. It seems that particles from
34 NBR compound penetrated into the interface region. As shown in Fig. 4 (a), the EDX line scan was
35 performed across the primary interface, with approximately 200nm thickness, between point A and
36 B. It is found that Si, Zn and O were concentrated in the interface region.
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38

39 As shown in Fig. 5 (a), the secondary interface had a similar microstructure feature as primary
40 interface. The observed thickness of interface was in a range of 300-500nm. Penetration of particles
41 from NBR compound into the interface region was observed in the secondary interface. EDX line
42 scan cross the secondary interface (Fig. 4 (b)) also agreed that Si, Zn and O were concentrated in
43 the interface region. It was noticed that concentration of Si, Zn and O across the secondary interface
44 had a bimodal distribution, whereas the analysed elements had a normal distribution across the
45 primary interface. However, the difference between distributions was not clearly understood, and it
46 is currently under further investigation.
47
48

49 In addition, precipitates were observed from PA6 in micro-cracks (Fig. 5 (b)). The size of
50 precipitates was in range of tenth of nanometers to few microns. As illustrated in Fig. 6 (a) and (b),
51 EDX analysis has shown that the precipitates and PA6 in micro-cracks contained Si and O, although
52 the intensity of Si peak from PA6 was very low. No Zn was detected in these regions. The
53 concentration of O and Si in the precipitates was 3-fold and 40-fold higher than the concentrations
54 in PA6 in micro-crack, as indicated in Fig. 6 (c). This result suggests that silane coupling agent
55 diffused from NBR compound into PA6 in micro-cracks and precipitated there once the PA6 was
56 over-saturated.
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1
2 It was not surprising that these precipitates were not observed in the bulk PA6 substrate. Since the
3 volume of PA6 in micro-cracks was much less than the volume of bulk PA6 substrate, the PA6 in
4 micro-cracks was more likely to be over-saturated by silane, compared with the bulk PA6 substrate.
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7 **4. Discussion**

8 **4.1 Formation of primary interface bonding**

9
10 At rubber vulcanization temperature of 150°C, PA6 substrate softening occurred, as the temperature
11 was above the glass transition temperature of PA6, 80 °C. In addition, the internal temperature of
12 NBR compound could be higher than the actual vulcanization temperature, since the rubber
13 vulcanization is an exothermic reaction. As a consequence, a localized melting of PA6 substrate
14 occurred at the contact surface of NBR compound/PA6 substrate.
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17
18 The proposed interactions taking place at the interface are illustrated in Fig. 7 (a) and (b). Firstly,
19 the penetration of hard silane modified nano-ZnO from NBR compound into soft or molten PA6
20 takes place due to the mechanical clamping. This is followed by the diffusion of silane on nano-
21 ZnO into PA6 substrate and subsequently the formation of hydrogen bonds between amide groups
22 and siloxane groups. The formation of such hydrogen bonding was noticed previously in another
23 study [7]. The hydrogen bonding enhances the bonding formed through the mechanical clamping.
24

25 **4.2 Formation of secondary interface bonding**

26
27 The generation of micro-cracks in NBR rubber compound could be induced by its thermal ageing or
28 it could be a result of internal residuals stress along the contact surface, due to the difference of
29 coefficient of thermal expansion between PA6 substrate and NBR compound, after the formation of
30 primary interface bonding. As long as the micro-cracks developed in NBR compound, the viscous
31 or molten PA6 flowed into the micro-cracks and led to the formation of secondary interfaces
32 between NBR compound and PA6. Similar to the formation of the primary interface bonding, the
33 secondary interface bonding developed through physical clamping and hydrogen bonding, as
34 illustrated in Fig. 7 (c) and (d). When PA6 in micro-cracks was over-saturated with silane, the
35 precipitates of silane formed.
36
37

38 **5. Conclusion**

39
40 When NBR compound vulcanized on PA6 substrate, two types of interface were observed, primary
41 interface and secondary interface. The primary interface developed through direct contact between
42 NBR compound and PA6 substrate. The generation of micro-cracks in NBR compound provided the
43 channels for secondary interface formation. The mechanism of interface bonding was proposed.
44 Interface bonding developed due to two interactions: physical clamping by penetration of hard
45 silane modified nano-ZnO into PA6; followed by the hydrogen bonding between silane and PA6.
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49 **References**

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52 [1] A. Y. Coran, *J. Appl. Polym. Sci.*, **2003**, 87, 24.
53 [2] P. Bindu, Sabu Thomas, *Polym. Eng. Sci.*, **2013**, DOI: 10.1002/pen.23383.
54 [3] P. Bindu, Sajeev Martin George, et al., *Society of Plastic Engineers*, **2013**, 10.2417/spepro.004655.
55 [4] Saeed Taghvaei-Ganjali, Mercedeh Malekzadeh, et al., *J. Appl. Polym. Sci.*, **2011**, 122, 249.
56 [5] S. MA, L. Shi, et al., *J. Shanghai Univ. (Engl. Ed.)*, **2008**, 12, 278.
57 [6] W. Ji, J. Hu, et al., *J. Appl. Polym. Sci.*, **2011**, 119, 1144.
58 [7] S. C. Tjong, *Materials Science & Engineering R*, **2006**, 53, 73.
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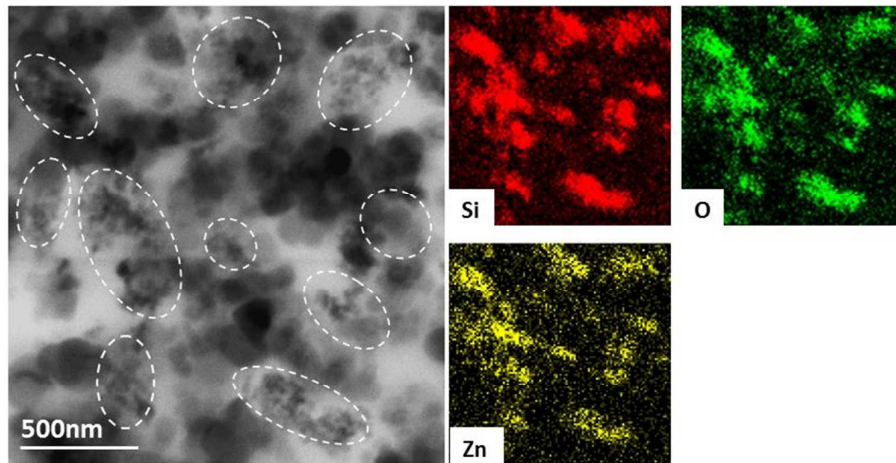


Fig.1 TEM bright field image of selected NBR compound, and EDX maps of Si, O and Zn.

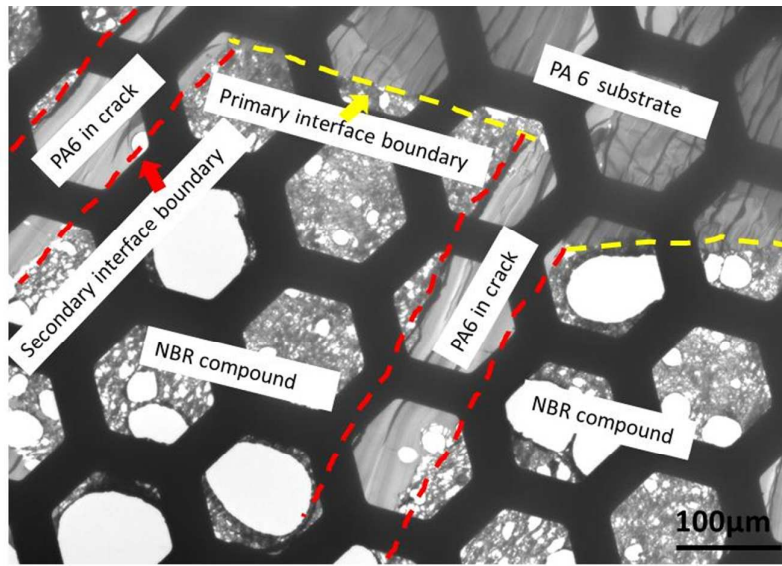


Fig.2 low magnification image of NBR compound/PA6 interface specimen on copper grids (primary interfaces boundaries were marked by yellow dashed line; secondary interfaces boundaries were marked by red dashed line)

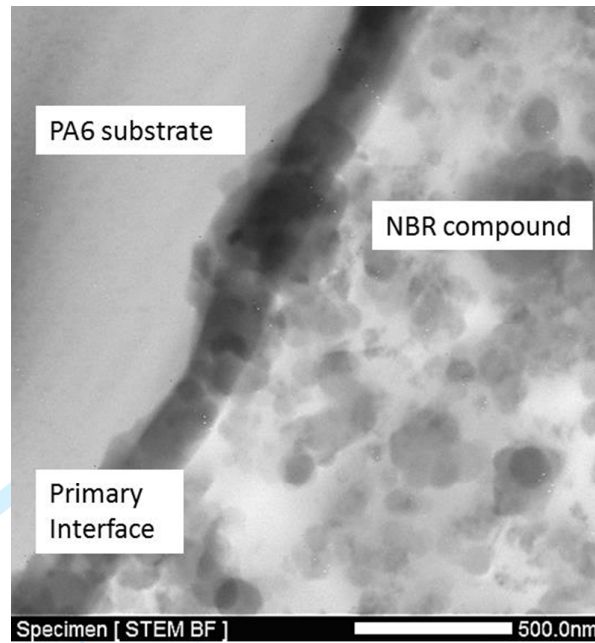


Fig. 3 TEM image of primary interface

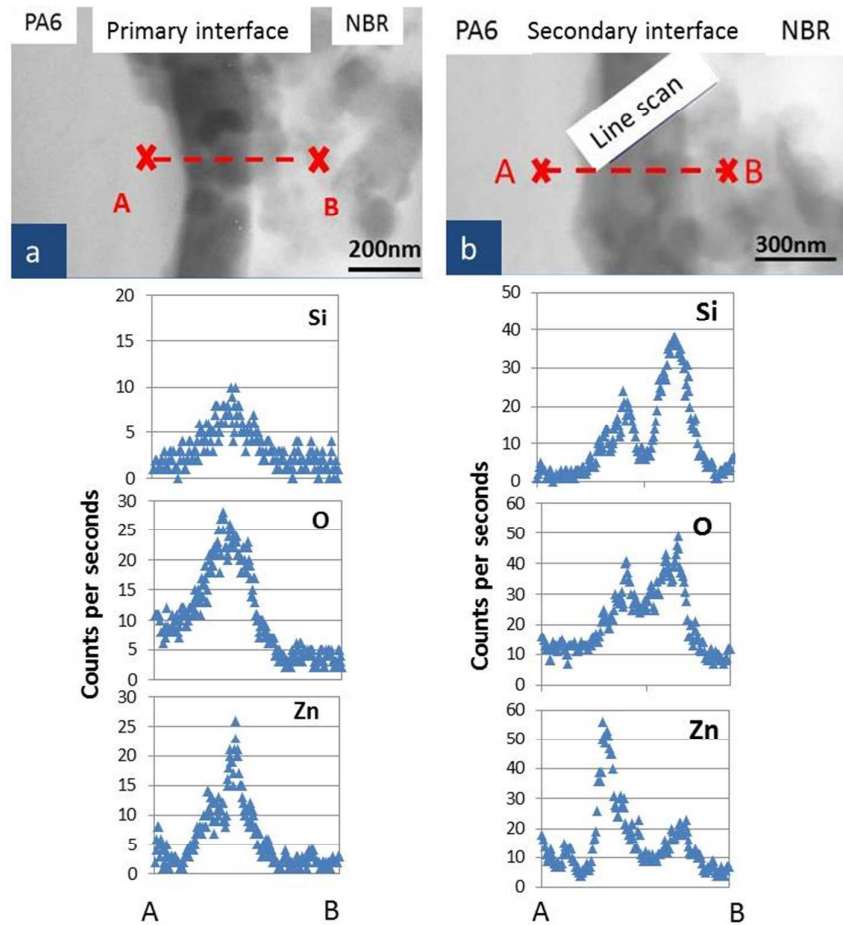


Fig. 4 TEM image and EDX line scan across (a) the primary interface and (b) the secondary interface between point A and B.

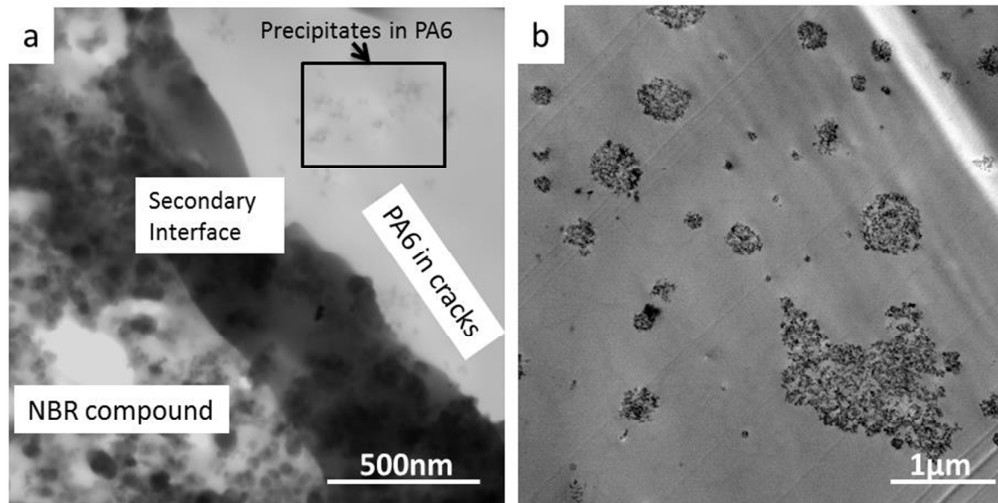


Fig.5 (a) TEM image of secondary interface (b) silane precipitates in PA6 in micro-cracks

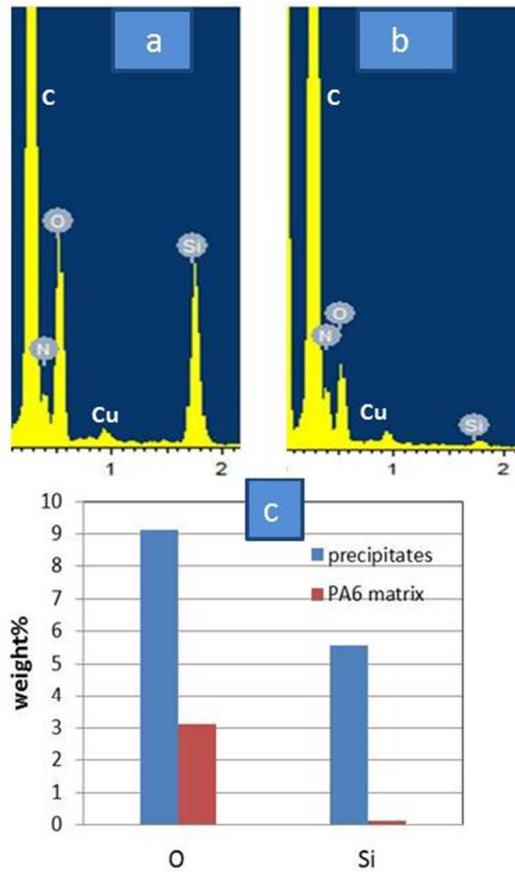


Fig.6 (a) EDX spectrum of precipitates, the Cu peaks were originated from the Cu grids (b) EDX spectrum of PA6 in micro-cracks,(c) the weight% of Si and O in precipitates and PA6 matrix.

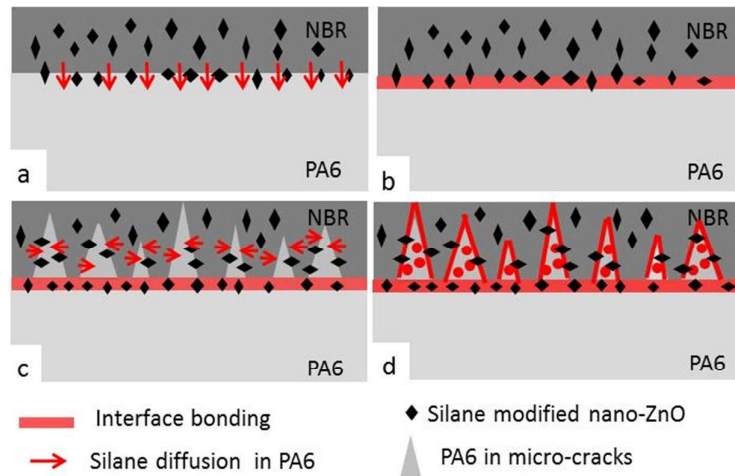


Fig. 7 Proposed mechanism of interfaces bonding formation (a) modified nano-ZnO penetration into soft or molten PA6, silane diffused into the substrate (b) Formation of hydrogen bonding on primary interface, (c) Silane diffused into PA6 in micro-cracks presented in NBR compound, (d) Formation of hydrogen bonding on secondary interface and silane precipitates