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Full Length Article

Hybrid joining of polyamide and hydrogenated acrylonitrile butadiene rubber through heat-resistant functional layer of silane coupling agent

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ABSTRACT

A simple, direct adhesion method was developed to join polyamide (PA6) to hydrogenated acrylonitrile butadiene rubber (HNBR) by grafting a functional layer of a silane coupling agent on plasma functionalized PA6 surfaces. The functional layer of the silane coupling agent was prepared using a self-assembly method, which greatly improved the heat resistance of PA6 from 153 °C up to 325 °C and the resulting PA6/HNBR joints showed excellent adhesion properties with cohesive failure between PA6 and HNBR. X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and nanoscale infrared microscopy and chemical imaging (Nano-IR, AFM-IR) were employed to characterize the surfaces and interfaces. The Nano-IR analysis method was employed for the first time to analyze the chemical structures of the adhesion interfaces between different materials and to establish the interface formation mechanism. This study is of significant value for interface research and the study of adhesion between resins and rubbers. There is a promising future for heat-resistant functional layers on resin surfaces, with potential application in fuel hose composite materials for the automotive and aeronautical industries.

1. Introduction

A composite laminated hose is suitable as a fuel conducting hose or diaphragm for use in the automotive and aeronautical industries. The structure is required to have an excellent heat resistance, gasoline permeation resistance, and low Freon gas permeability while maintaining suitable adhesion and flexibility properties [1]. Nowadays, laminated hoses are mostly comprised of resin layers and adjoining rubber layers. Hydrogenated nitrile butadiene rubber (HNBR) is widely known for its physical strength and retention of properties even after long-term exposure to heat, oil, fuel, and other chemicals; hence, it is widely used in the automotive and aeronautical industries as the inner and outer layers of fuel and oil handling hoses to ensure connection-pipe sealing and low fuel permeability [2]. A fluorine-containing resin is normally used in multi-layer hoses as a fuel barrier layer. There is a trend towards building thickened layer to ensure the fuel barrier property against ethanol-blended gasoline, which is being widely used to address environmental concerns. However, thickened fuel barrier layers degrade the hose flexibility, workability, and compatibility [3]. Additionally, the fluorine-containing resin and the rubber layer face adhesion problems and the adhesive agents can also affect the peripheral component parts [4]. Therefore, it has been proposed to build multi-layer hoses with an intermediate layer that includes a resin connected with rubber materials, and provides a fuel-proof barrier property.

Polyamide 6 is known for its low Freon gas permeability, fluorine impermeability, moisture impermeability, and rigidity [5,6]; furthermore, it can facilitate a thinner barrier layer than those in conventional hoses using a fluorine-containing resin [3]. The polyamide adhered to the HNBR multi-layer hose guarantees flexibility and workability. However, the polyamide resin has a lower heat resistance than the fluorine-containing resin and it does not bond well with the HNBR surface because of their different solubility parameters. In the literature, adhesives such as a solvent-type phenolic resin, a mixed solvent of a phenolic resin and an elastomer, or an epoxy resin adhesive were used to bond these two materials [6]; however, this process requires long processing times, causes spew and extra adhesive problems, and is quite costly [7]. Additionally, the bonding via adhesive application is mainly due to van der Waals' forces [8]; the adhesion strength is not enough to withstand the stresses generated in working conditions, thus resulting in interface adhesive failure. In order to enhance the efficiency of the PA6 resin in a composite laminated hose, it is proposed

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to improve its heat resistance and the adhesion between PA6 and HNBR.

Silane coupling agents based on aminopropylalkoxysilanes are widely used as grafting agents to promote the interfacial behavior in many devices, owing to their heat resistance property and bifunctional nature [9,10]. The presence of the amine functionality results in aminosilanes with unique properties. These amine groups can catalyze, either by an inter- or an intra-molecular process, the reaction between the silane molecules and the surface hydroxide and/or silanol groups to form siloxane linkages [11,12]. Therefore, the active use of the bifunctional property of the aminopropylalkoxysilanes is important to encourage reactions between the rubber and amine groups, and the silanol groups and resin substrates, for achieving hybrid linkages between the HNBR and PA6. In the past, the adhesion of PA6 and HNBR was investigated by several methods, including the usage of silane-modified nano-ZnO during sulfur curing, the carboxylation of rubber, and the addition of adhesion promoters in the rubber matrix [13–15]. These methods do improve the adhesion between PA6 and HNBR; however, the rubber composition and its original properties were altered since additives were blended into the rubbers. Additionally, there is little information available on the mechanism of interface formation between the resin and the rubber.

In this study, we focus on building a hybrid link between PA6 and HNBR by using a functional layer of 3-aminopropyltrimethoxysilane (APTMS). Here, an APTMS functional layer was prepared on a plasma functionalized PA6 surface and subsequently HNBR was reacted with the APTMS-linked PA6 during the curing process. The chemical and thermal surface properties were characterized by X-ray photoelectron spectroscopy (XPS) and nano-thermal analysis (Nano-TA). The adhesion and heat-resistance mechanisms of APTMS at the interface between PA6 and HNBR were investigated by transmission electron microscopy (TEM) and Nano-IR. This research can potentially help develop functional layers with better performance for resin and rubber joints, composite materials, and laminated hose applications with great benefits in terms of the thermal characteristics, cost, and processing stability.

2. Experimental

2.1. Materials and reagents

HNBR (acrylonitrile: 36.2%, Zetpol 2020L, Zeon Co., Japan) was used in this study. The NBR compounds were prepared using a Banbury mixer to mix HNBR (100 phr) with additives – carbon black (75 phr), zinc 2-mercaptobenzimidazolate (1 phr), 4,4′-bis(α,α-dimethylbenzyl)diphenylamine (1 phr), stearic acid (1 phr), and ZnO (5 phr) as a stabilizer. Diisononyl adipate (5 phr), Sumikanol 620 (3 phr, modified resorcinol formaldehyde resin), Sumikanal 507 (3 phr, modified melamine resin), trimethylolpropane trimethacrylate (1.5 phr), and bis(*tert*-butyldioxyisopropyl)benzene (7.5 phr) were added to the aforementioned base compounds as curing agents using a kneader and an open two-roll mill.

The resin used in this study was a polyamide (PA6, 1013NW8, UBE Co., Japan). The silane coupling agent, 3-aminopropyltrimethoxysilane (APTMS), and ethanol were procured from Wako Pure Chemical Industries Co. Ltd., and were used without further purification.

2.2. Grafting of the APTMS functional layer on the PA6 surface

The PA6 surfaces were pre-treated by plasma radiation before APTMS functional layer fabrication. Prior to the plasma treatment, the PA6 substrates were washed in an ultrasonic bath with ethanol for 10 min and then dried at 80 °C for 24 h. A plasma reactor (Pico powder treatment, Diener Electronic Co., Japan) was used to functionalize the PA6 substrates. The PA6 plates were fixed in the reaction chamber, which was vacuumed and then filled with an Ar inert gas. Plasma was generated at a given pressure (0.4 mbar) and the PA6 substrates were exposed to plasma radiation for a predetermined period of time. The obtained PA6 was immersed in APTMS (1, 3, 20 wt.%) aqueous solution at 25 °C for 1 s, and then dried in air.

2.3. HNBR curing and HNBR/PA6 process

HBNR obtained after open-mill mixing was cured using a molding process that involves contact with the APTMS-linked PA6 in a molding cabinet at 170 °C (8 MPa) for 20 min. After the molding process, the cured HNBR samples were immediately removed from the molding cabinet. Cross-sectional samples of the cured HNBR rubbers were prepared for analysis. Before surface analysis, the APTMS-linked PA6/HNBR joint samples were kept in air for 24 h.

2.4. Characterization

Static contact angles were measured by an optical contact angle measuring instrument (G-1, Erma Inc.) with droplets (1 μL) of distilled water at 25 °C. The contact angle was measured at six different positions on each sample; the average of these values is reported as the contact angle.

The surface chemical composition and structure of PA6 after plasma treatment and APTMS functional layer grafting were analyzed by XPS (PHI QUANTERA ESCA system) using a Multi Technique spectrometer with a focusing monochromator (ULVAC-PHI Inc.) and an Al Kα X-ray source (φ 100 μm spot) for surface analysis. The pass energy of the analyzer was 69 eV for high-resolution scans at 300 W. The angle resolved measurements were carried out at an electron take-off angle of $\theta = 45^\circ$. The analysis chamber remained at 3.0×10^{-6} Pa during the whole XPS measurement range under charge neutralization. The XPS spectra were subjected to the Shirley background subtraction formalism, and the data of the saturated C1s peak at 284.8 eV were used in assigning the chemical-bonding states. During the curve-fitting treatments, Gaussian-Lorentzian lines of variable proportion were used; the XPS experimental curve fitting was performed using the Multipak software.

Local thermal analyses were performed by a nano-thermal analysis VESTA system (Model Nano-TA2, Anasys Instruments Corporation Co. Ltd.). The thermal probes (Model EX-AN2-300, Anasys Instruments Corporation Co. Ltd.) used for local thermal analysis had spring constants of ~0.1–0.5 N/m, tip radii <30 nm, and upper limit temperatures of 400 °C. The measurements were taken at five points on every sample at a heating rate 10 °C/s.

The strengths of the PA6/HNBR joints were determined using a T-peel test. PA6/HNBR joints were fabricated using two similarly treated strip test pieces (60 mm × 10 mm). The joints were maintained at 25 °C for 24 h before performing the T-peel test, which was carried out on a tensile machine (IMADA Co. Ltd., mX-2500N) according to the 90° type peeling test at a crosshead speed of 50 mm/min at 25 °C.

The interface morphologies and structures of the PA6/HNBR joints were characterized by a transmission electron microscope (TEM, JEM-2100, JEOL Japan, operated at 200 kV) equipped with an X-ray electron microprobe for energy-dispersive X-ray spectroscopy (EDS). For TEM measurement, the samples were prepared on a microtome (Leica Ultracut).

We used a Nano-IR platform (Nano-IR EasyScan 2 AFM, Nanosurf AG Co.) for the nanoscale infrared measurements that combines a high-resolution and low-noise AFM with a tunable infrared laser.