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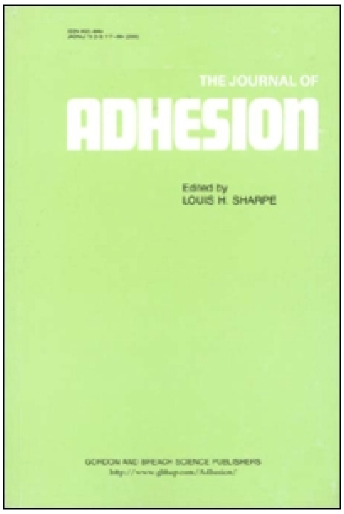

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# Effect of In Situ Polymerization of Styrene onto Natural Rubber on Adhesion Properties of Styrene-Natural Rubber (SNR) Adhesives

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*Styrene-based deproteinized natural rubber (SNR) latex was synthesized by* in situ *polymerization. Three pre-vulcanization systems [conventional-cured (CV), semi-efficient-cured (Semi-EV), and efficient-cured (EV)] were studied in terms of tensile and adhesion properties. Good tensile properties were observed for CV and EV SNR. The Semi-EV SNR showed the best adhesion properties based on the good anchorage performance in all substrate pairings (polystyrene–polystyrene, polystyrene–rubber, and rubber–rubber). The pH modification on SNR latex* via *KOH addition has beneficial effects of removing protein layers, resulting in more styrene grafting sites in the rubber molecules. Consequently, the tensile and adhesion properties of the SNR are improved as more styrene polymers are grafted onto the rubber matrix. Semi-EV SNR with pH 12 has superior adhesive performance; hence, it is suitable for use as a pressure-sensitive adhesive.*

**Keywords:** Polystyrene; Pressure-sensitive adhesive; Styrene-based natural rubber; Sulfur

## 1. INTRODUCTION

Adhesives are widely applied in domestic households, automotives, electronic devices, aerospace, and other industries. The basic applications of adhesives are for glueing ceramics, composites, plastics, rubbers, woods, and metals to themselves or to each other. Two of

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the major adhesives in the market are pressure-sensitive adhesives (PSAs) and hot melt adhesives. According to Rolando [1], the current trend in hot melt adhesives is to dilute a typical polymer solid with other different components to complement and improve the adhesive. For instance, high molecular weight polymer and low molecular weight resin are blended to achieve a balanced set of properties. PSAs are viscoelastic materials with the potential to adhere to substrates with minimum pressure over a short period of time. In the 19th century, the discovery of natural rubber as the first solvent-based PSA and its usage had been widely recognized in the tape and label industries. Recently, the control of adhesive properties through structured particle design of water-borne PSAs has been studied by Foster *et al.* [2]. For further improvement of the joint strength, the mixed adhesive joint technique can offer a good combination of strength and toughness [3].

Nanocomposite PSAs are among the new growth adhesive materials. Kajtna and Sebenik [4] reported the synthesis of acrylic polymer/montmorillonite (MMT) clay nanocomposite PSAs by suspension polymerization. They designed a new water-soluble PSA for medical-grade application by mixing polyisobutylene (PIB) and sodium carboxymethylcellulose (CMC). Both are physiologically inert and yield a special moisture-absorbing PSA, and thus are suitable for medical application as patch preparations [5]. The rheological properties of PIB and CMC have already been investigated [6]. Polymers used as PSAs are mostly styrene block copolymers, natural rubber, polyacrylate, random polymer styrene-butadiene rubber, or butyl rubber [7,8]. For example, carboxylated styrene-butadiene rubber and styrene-butadiene rubber are used as bases for PSAs and styrene-2-ethyl hexyl acrylate copolymer containing 14 mass% of styrene is used as a PSA modifier [9].

Earlier work has been done on the grafting efficiency of styrene onto deproteinized natural rubber latex using proton-nuclear magnetic resonance analysis, Fourier transform Infrared analysis, and sol-gel method [10].

This work focuses on the properties of a PSA based on styrene deproteinized natural rubber (SNR). It is intended to improve the properties of the SNR-based PSA by using three different curing systems, namely conventional vulcanization (CV), semi-conventional vulcanization (semi-EV), and efficient vulcanization (EV) with varying pH values of the SNR adhesive. In many cases, different substrate surfaces are to be adhered with an adhesive. Thus, the anchorage properties of the SNR adhesive on various substrates, such as polystyrene (PS) and natural rubber (NR), PS–PS, and NR–NR pairings, were investigated. A dead load test was carried out to evaluate the performance of the adhesive and the outcomes such as maximum load-to-fail, average time-to fail, and anchorage, were used as performance indicators for the SNR adhesive. The term "anchorage" is defined as the level of adhesion, that the adhesive has on its own carrier/backing [11]. It is mostly used in the tape industry, where good anchorage ensures that the tape would not transfer its adhesive to the intended substrate completely, causing a delamination failure in the tape. In this work, the term anchorage refers to the ability of the adhesive to adhere to the substrates evenly.

## 2. EXPERIMENTAL

### 2.1. Materials

Deproteinized Natural Rubber (DPNR 1101) latex was supplied by Sumirubber Industries (M) Sdn. Bhd. (Sungai Petani, Malaysia). Styrene monomer and the initiator used, ammonium persulfate $(NH_4)_2S_2O_8$, were purchased from Fluka Chemical Company (M) Sdn. Bhd. (Kuala Lumpur, Malaysia). The chemicals used for SNR were antioxidant [AOX] (butylated reaction product of p-cresol and dicyclopentadiene), potassium oleate, zinc-diethyldithiocarbonate (ZDEC), sulfur, zinc oxide (ZnO), and potassium hydroxide (KOH), which were purchased from Anchor Chemical Co. (M) Ltd (Mumbai, India).

### 2.2. Preparation of SNR Samples

For pure polymerization of styrene onto DPNR latex, a reactor model RE162/P (IKA-Labotechnik, Staufen, Germany) was used. The emulsion polymerization of styrene in DPNR latex involved adding water, latex, monomer styrene, and initiator according to the recipe illustrated in Table 1. The emulsion polymerization of styrene in DPNR latex was carried out according to the method reported previously [12].

**TABLE 1** Recipe for Emulsion Polymerization of Styrene in DPNR

| Recipe | Amount (g) |
|---|---|
| DPNR latex | 100 |
| Styrene monomer | 19.7 |
| Initiator | 0.394 (2 wt.% styrene) |
| Distilled water | 77.0 |

**TABLE 2** Recipe for Pre-Vulcanization Systems of SNR Latex

| | Weight (*phr) | | |
|---|---|---|---|
| Ingredients | EV | Semi-EV | CV |
| SNR latex | 100 | 100 | 100 |
| Sulfur | 0.3 | 1.5 | 2.5 |
| ZDEC | 2.5 | 1.0 | 1.0 |
| Zinc oxide | 5.0 | 5.0 | 5.0 |
| Antioxidant | 1.0 | 1.0 | 1.0 |
| Potassium oleate | 1.0 | 1.0 | 1.0 |

*phr: parts per hundred rubber.

The polymerization temperature used was 60°C with a stirring speed of 180 rpm. The emulsion polymerization was carried out for 9 h. The recipe for the pre-vulcanization system of the SNR latex is shown in Table 2. After the elapsed polymerization time, the pre-vulcanization ingredients as indicated in Table 2 were added into the SNR latex reactor with the stirring speed of 180 rpm and temperature of 60°C until chloroform number two was observed. The coagulum properties were based on previous work reported by Blackley [13]. The SNR latex is extracted from the flask and left to mature for 2 h at room temperature. To investigate the bulk mechanical properties of the SNR adhesive, the SNR latex was cast on a glass tray and allowed to cure at room temperature for 48 h.

## 2.3. Differential Scanning Calorimetry Analysis of SNR and Pure DPNR Samples

The SNR (subjected to 9 hours of polymerization time) and pure DPNR latex are dried at room temperature for 48 hours. Then small portions of 5 grams each are extracted from both samples and subjected to DSC analysis using a Perkin Elmer (Model DSC7, Eden Prairie, MN, USA). The parameters for the test are heating rate of 10.0°C/min, temperature range of −100 to 150°C and using nitrogen gas.

## 2.4. Tensile Test of SNR Samples

The SNR films were cut into a dumbbell shape and a tensile test was carried out according to ASTM D412-B. A Universal Instron Tester

(Instron, Canton, MA, USA) with the crosshead speed of 500 mm/min was used to investigate the tensile properties. To investigate the pH effect, 10% of KOH was added drop by drop to the SNR latex and the corresponding changes in pH values were recorded using an electronic pH meter. A range of pH values from 10 to 14 were studied and the best pH value with the optimum curing condition was used. After the optimum pH is determined, the amount of KOH needed to obtain that pH will be added during the pre-vulcanization phase after the grafting process of SNR for all subsequent batches of pre-vulcanized SNR latex.

## 2.5. Adhesive Tests for Cured SNR

The SNR latex with curatives were applied on the surface of the PS–NR, PS–PS, and NR–NR substrates. The substrates pairings that were adhered by the SNR adhesive were left to cure for 48 hours under a constant load of 2 kg. For comparison purposes, envelope adhesives based on a commercial recipe (model number LS-OPP-B002C-1, Liao Sheng Trading Company, China) but based on DPNR latex was used on the substrate pairings. The comparison was made with the envelope adhesive as it uses the same DPNR latex base as the SNR adhesive. Table 3 shows the recipe for the envelope adhesive.

A modified T-peel test according to ASTM standard D1876 was used to determine the performance of the SNR adhesive. The modified version used a dead load test to determine the amount of load needed to fail the adhesive. One end of the unadhered substrate was suspended from a clamp, where another weight was added to other end of the substrate in increments of 50 grams until a steady peeling of the bonded substrates were noticeable. More weights were added when the peeling of the substrates ceased. The maximum load, the average time-to-fail, and the anchorage of adhesive to the substrate were recorded.

**TABLE 3** Recipe for Envelope Adhesive

| Ingredient | Wet weight ($^{\#}$phr) |
|---|---|
| 60% DPNR latex | 100 |
| 10% KOH solution | 1.2 |
| 50% ZDEC | 0.6 |

$^{\#}$phr: parts per hundred rubber.

$^{*}$The DPNR used is from the same source for SNR latex.

## 3. RESULTS AND DISCUSSION

### 3.1. Thermal Properties Analysis: Differential Scanning Calorimetry

DSC spectra of DPNR and SNR (9H) are shown in Figs. 1 and 2, respectively. In Fig. 1, the DPNR sample showed only one $T_g$ peak of NR at −61.6°C. For the SNR sample as shown in Fig. 2, the rubber peak is clearly observed at a temperature of −61.6°C, which is similar to the $T_g$ of pure DPNR rubber. However, the SNR9H sample also shows two additional peaks, although not so pronounced, at approximately 65 and 105.3°C. The higher $T_g$ (105.3°C) peak corresponds to the $T_g$ of Polystyrene in SNR9H. The PS-grafted DPNR portion is expected to produce the intermediate $T_g$ peak (corresponding 65°C) in this analysis, which proves good compatibility of the rubber (DPNR) and polymer (PS) molecules in the grafting process.

### 3.2. Effects of the Three Pre-Vulcanization Systems on the Tensile Properties of SNR Latex

Figures 3, 4, and 5 show significant improvements in the tensile properties of all three pre-vulcanization SNRs, compared with pure SNR. The binding effects of the sulfur crosslinks on the molecular chain of the rubber restrict the slippage of the molecular chain of

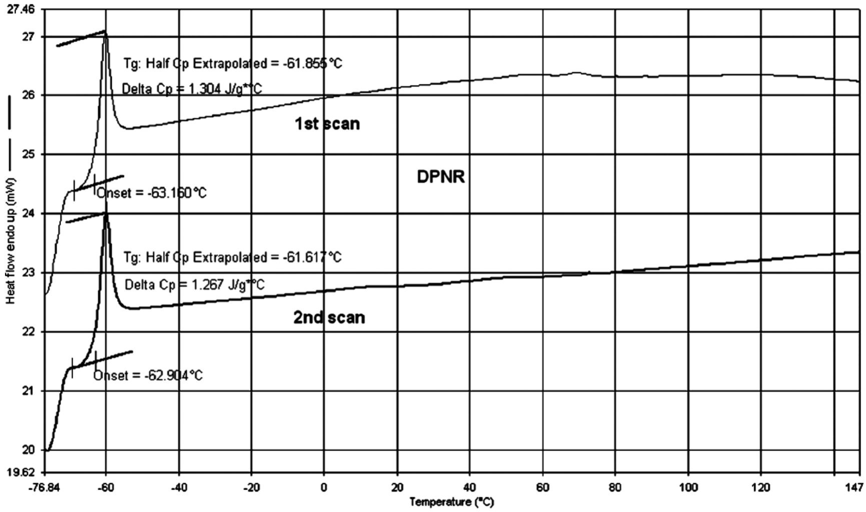


**FIGURE 1** DSC spectrum of pure DPNR.

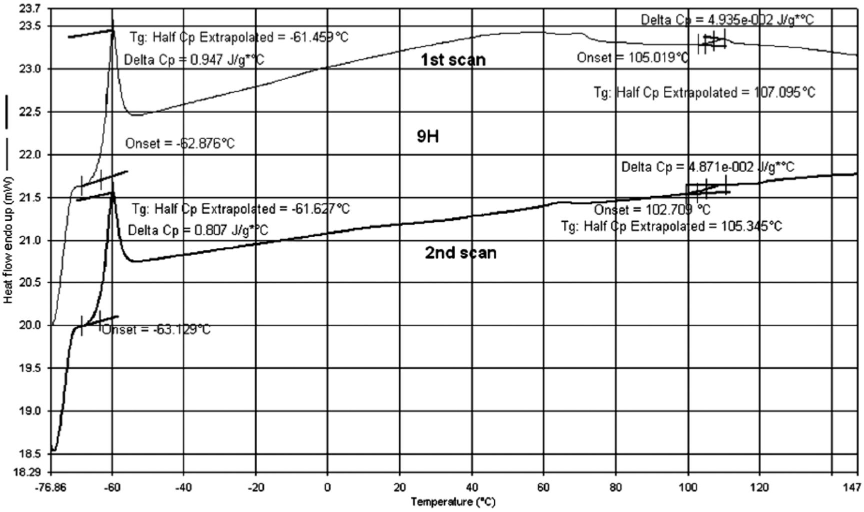


**FIGURE 2** DSC spectrum of SNR (9 hours of polymerization).

the rubber from occurring during bulk deformation of the rubber. Che Man and Hashim Akil [14] reported that sulfur crosslinks can withstand more stress before chain breakage and the crystallization effect during tensile loading will increase the elongation at break (EB). The CV-vulcanized SNR latex had the highest tensile strength (TS) while the EV-vulcanized SNR latex showed the highest elongation at

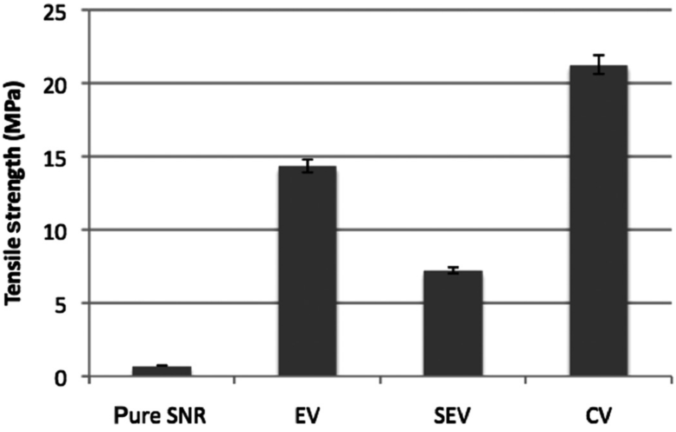


**FIGURE 3** Tensile strength of the pre-vulcanization SNR latex.

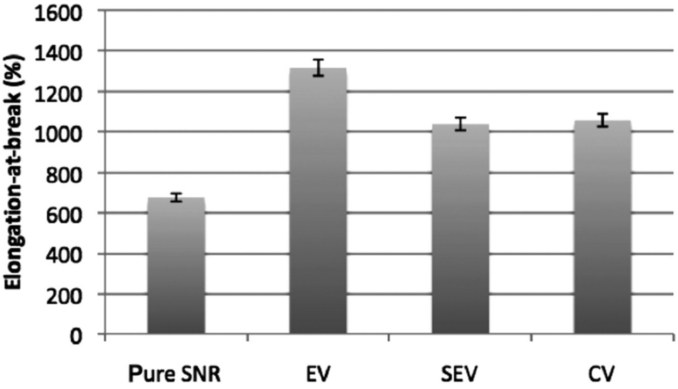


**FIGURE 4** Elongation at break of the pre-vulcanization SNR latex.

break (EB). Previous work by Azura *et al*. [15] has been done on the sulfur crosslink characterization of the unfilled rubber vulcanizates, which reported that the crosslink densities of the CV, semi-EV, and EV vulcanizates were 139, 145, and 151 $mol/m^3$, respectively. The CV system had relatively long polysulfuldic crosslinks, and thus required more energy to scission, and strain hardening of the sulfur crosslinks may happen [13]. This statement agrees with the result shown in Fig. 5, that is, the CV system has the highest TS and modulus. For the EV system, owing to the high accelerator content, more active sites formed on the rubber chain. Thus, shorter sulfur crosslinks (mainly monosulfudic or disulfidic) generated uniform deformation of the bulk rubber before plastic deformation occurred,

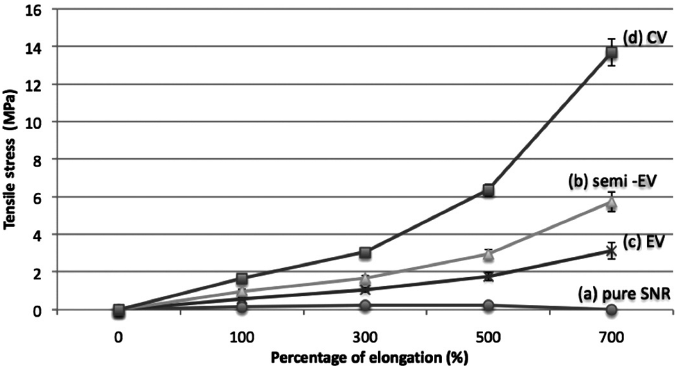


**FIGURE 5** Stress-strain curves of the SNR rubber of (a) pure SNR, (b) semi-EV, (c) EV, and (d) CV pre-vulcanized systems.

resulting in higher EB. The semi-EV system showed the same trend in the EB compared with the CV system; however, the TS was the lowest among the three pre-vulcanized systems. The factors to be considered are the localized stress concentrations in certain areas of the bulk rubber chain owing to the broad distribution of the sulfur crosslinks (mono, di, or poly-sulfidic) lengths. The EB of the semi-EV system was comparable with the CV system. In this case, the existing partial short crosslink chain may have contributed to some degree of strain hardening of the rubber. This statement is supported by similar findings by Hourston and Romaine [16] on the modification of NR with styrene. Based on the results, the semi-EV system was chosen for the investigation of the effect of KOH loading for different pH values of the SNR latex.

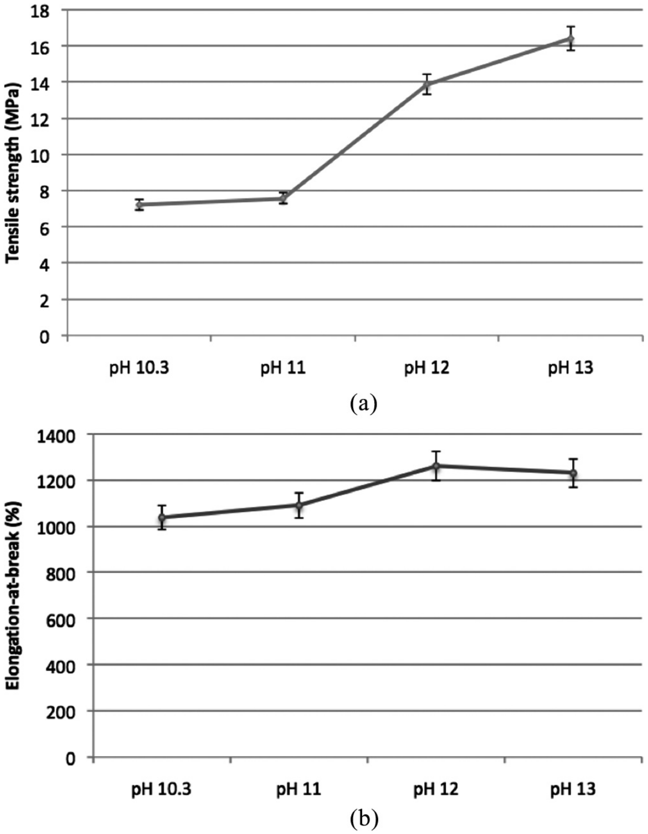
## 3.3. The Effect of pH Modification on Semi-EV SNR Latex

The tensile properties with different pH values (11, 12, and 13) of the SNR latex were investigated and compared, without any KOH modification, with semi-EV SNR latex with pH value of 10.3.

Figure 6 shows that the trend of TS and EB of semi-EV SNR are growing upward. The growth of TS is more pronounced than that of EB. Based on the Brock *et al.* report [17], when the latex was in an alkaline medium, the protein layer of the latex structure will undergo a hydrolysis process. Protein will also be further removed from the SNR latex owing to bacterial action or side reaction, which increases the active sites on the rubber chain to perform further grafting and crosslinking. The reduction of protein was low at pH 10, while at a higher pH value, the hydrolysis process was more pronounced [14]. The semi-EV SNR with higher pH value was assumed to have achieved higher grafting efficiency and, subsequently, would improve the TS of semi-EV SNR. In the case of EB, a small amount of protein within the SNR latex will react like a binder and further impart a certain degree of stiffness [18]. After removal of the protein, the latex chains gained flexibility, thus EB was increased. However, the highly grafted styrene and sulfur crosslinking on the rubber chain in the compound with pH 13 destroyed the chain flexibility and thus reduced the EB value.

## 3.4. Effect of SNR Formulation on Adhesive Performance

By using the PS-NR substrate, the adhesion performances of SNR latex with different pre-vulcanization systems were compared with the envelope adhesive. Figure 7 shows improvement in maximum



(a)

(b)

**FIGURE 6** Effect of pH on the (a) tensile strength and (b) elongation-at-break of the Semi-EV SNR latex.

loading for all SNR formulations compared with the envelope adhesive. The CV SBNR latex has the higher maximum load performance compared with the envelope adhesive. This is due to the grafting effect of styrene on the rubber chain, which acts as a surface compatibilizer. The compatibilizing effect contributed by the polystyrene resin [19] may modify the viscoelastic properties of the adhesive. The envelope adhesive has no such modifier to upgrade its viscoelastic properties, thus its maximum loading performance was the lowest.

Figure 8 shows a mixed trend in the average time-to-fail. Both pure SNR and EV SNR latex have higher average time-to-fail, while the semi-EV and the CV SNR latex showed a reduced trend in the same parameter as compared with the envelope adhesive. In this case, a

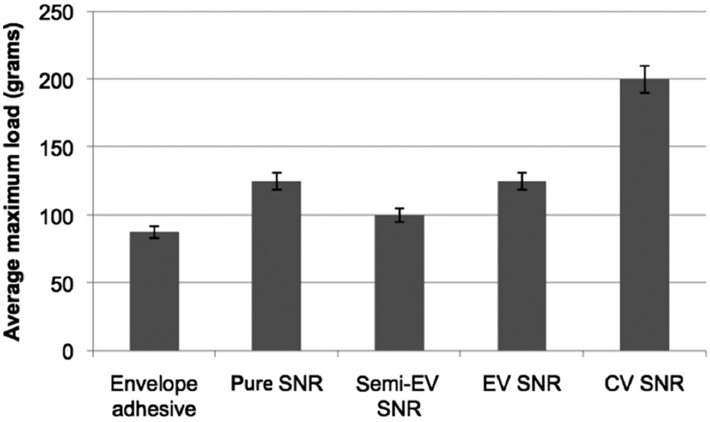


**FIGURE 7** Mean maximum load supported by various adhesive formulations.

shorter sulfur crosslink is favored to generate uniform deformation in the bulk rubber, thus the average time-to-fail performance of EV SNR is better. A similar trend is noted in Fig. 4 which shows that the EB is the highest among the three pre-vulcanization SNRs. For pure SNR, the effect of grafted styrene is more pronounced without the sulfur crosslink network, thus the average time-to-fail performance is better compared with semi-EV and CV SNR.

Based on the results shown in Table 4, the semi-EV SNR latex adhesive has excellent anchorage ability, meaning that it adheres evenly to both sides of the substrates. This phenomenon showed a

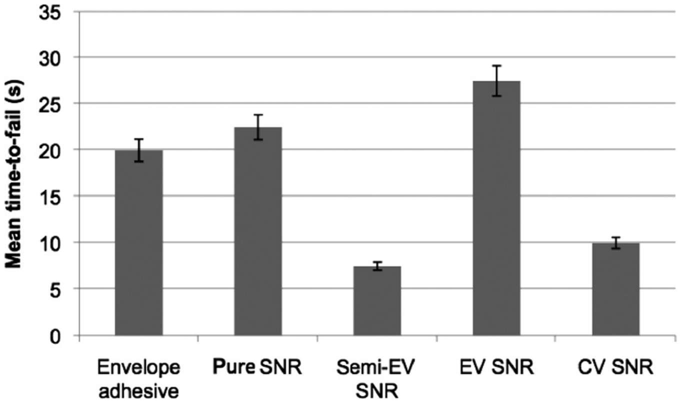


**FIGURE 8** Average time-to-fail for various adhesive formulations.

**TABLE 4** Anchorage of Various SNR Adhesive Formulations

| Adhesive formulation | Anchorage |
|---|---|
| Envelope adhesive | Poor |
| Pure SNR | Poor |
| Semi-EV-cured SNR | Good |
| EV-cured SNR | Poor |
| CV-cured SNR | Poor |

different trend, compared with maximum load performance, which is the lowest among the three pre-vulcanization systems. The broad distribution of the sulfur crosslinking network within the semi-EV SNR latex is the main factor that improves the anchorage performance of the semi-EV SNR adhesive. Another point of view is the compatibility of SNR latex base adhesive with the NR and PS substrates, which improves the anchorage performance for both substrates. There is a more varied length of the sulfur chain within the semi-EV SNR adhesive, thus the adhesive has a fair wettability on both surfaces of the NR substrate and the PS substrate. Table 5 compares the failure initiation loads and failure types for the semi-EV cured latex of pH 12 with the envelope adhesive.

## 3.5. Effect of pH of SNR Latex on Adhesion Performance

By using all three substrates pairings, the effects of different pH values on semi-EV SNR latex adhesive are summarized in Figs. 9 and 10 and Table 6. At pH 12, semi-EV SNR latex adhesive showed the highest maximum load, average time-to-fail, and anchorage performance. Goettlich-Riemann *et al.* [20] has done some work on

**TABLE 5** Effect of pH on the Anchorage of the Semi-EV SNR Latex Adhesive

| pH | Anchorage |
|---|---|
| pH 11 | Fair |
| pH 12 | Good |
| pH 13 | Fair |

Anchorage performance indicators:.

Fair—Adhesive failure results in deposition of adhesive mostly on one side of the adhesive.

Good—Adhesive failure results in deposition of adhesive on both sides of the substrates evenly.

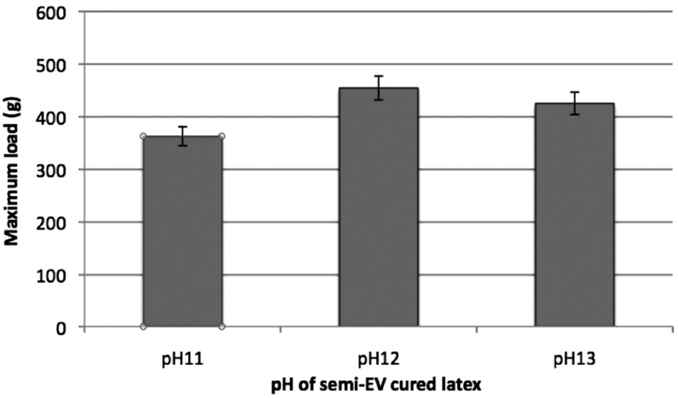


**FIGURE 9** Effect of pH modification on the maximum load of the SNR adhesive.

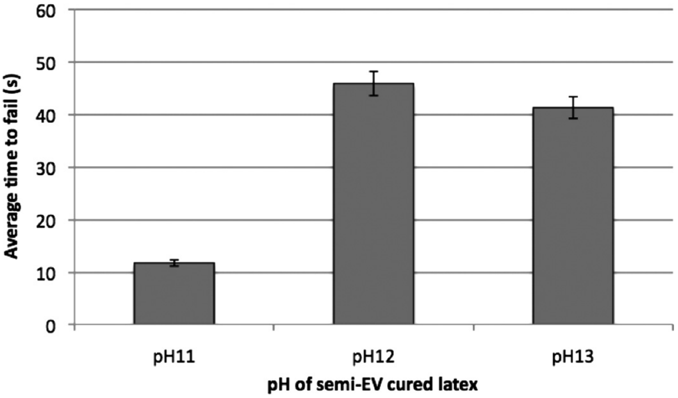


**FIGURE 10** Effect of pH modification on the average time-to-fail of the SNR adhesive.

**TABLE 6** Failure Initiation Loads and Failure Type of SNR Latex Adhesive and Envelope Adhesive

| Adhesive | Substrate pairing | Average failure initiation load (g) | Failure type |
|---|---|---|---|
| SNR adhesive (semi-EV, pH 12) | PS – DPNR | 75.0 | Adhesive |
| | PS – PS | 100.0 | Adhesive |
| | DPNR – DPNR | 1100.0 | Adhesive |
| Envelope adhesive | PS – DPNR | 50.0 | Cohesive |
| | PS – PS | 150.0 | Cohesive |
| | DPNR – DPNR | 900.0 | Adhesive |

the effect of pH on protein hydrolysis. Similar findings has been reported by Maznah *et al.* [21]; that is, the increase in KOH content will remove more protein within the rubber particles. Hence, more active sites for styrene grafting and sulfur crosslinking are available. Higher grafting means more styrene in the rubber chain, thus more adhesive input, which leads to optimum adhesion properties at pH 12. Though the KOH has improved the adhesion properties at pH 12, the further input of KOH in semi-EV SNR adhesive will tend to result in a negative trend. In as much as a higher degree of sulfur crosslinking means an increase in rigidity, the restricted movement in the rubber chain reduces the adhesion performance [21].

## 4. CONCLUSIONS

Compared with the commercial envelope adhesive, all SNR latex formulations showed improved maximum load, average time-to-fail, and anchorage performance. Pure SNR latex has the maximum load that contributes to enhanced effectiveness of polystyrene as an adhesion enhancer. For pre-vulcanization SNR latex, the sulfur crosslinking network successfully improved the tensile properties. However, the rigidity of the sulfur crosslinking network reduced the efficiency of the SNR latex as an adhesive. Semi-EV SNR showed good anchorage to all substrate pairings. The semi-EV SNR latex with pH 12 was the optimum KOH loading, which gave superior adhesion properties in the semi-EV-SNR latex adhesive.

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