

Influence of Thermal and Oil Aging on Weldline Strength of NR/EPDM and NR/NBR Blends

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ABSTRACT

Weldline is one of the typical molding defects and appears at the meeting points of multiple melt flows. The presence of weldlines in rubber products is regarded as one of the most undesirable phenomena, since it may result in poor mechanical properties as well as surface appearances. Compression moldings of large or complicated products are usually prepared by multiple charges, which produce weldlines once the melt fronts are joined by impingement flow. In the present study, ethylene propylene diene monomer and acrylonitrile butadiene rubber were blended into natural rubber (NR) in order to enhance the aging properties with respect to the heat, oil and ultraviolet resistances of an NR specimen containing a weldline.

Keywords: weldline strength, rubber blends, compression molding process

INTRODUCTION

Weldlines are formed when two or more polymer melt flows meet in a cavity. As a result, the presence of a weldline reduces the mechanical strength and also affects the surface appearance of the final product. Designers typically minimize the influence of weldlines by locating them in non-critical areas and using a safety factor based on design specifications and anticipated failure modes. This practice can result in the over-design of parts since the safety factor is, in general, independent of the material. Truly cost-effective part design requires a better understanding of the behavior of polymers under different loads and failure conditions. A large amount of literature (Malguarnera and Manisali, 1981; Vaxman *et al.*, 1991; Bevis *et al.*, 1998; Kühnert *et al.*, 2005;

Patcharaphun *et al.*, 2006; Zhou and Mallick, 2006) has been published concerning the effects of weldlines on the mechanical properties of injection-molded thermoplastics and thermoplastic composites. In order to increase the weldline strength of injection-molded parts, especially for injection-molded thermoplastic composites, some special injection molding techniques have been developed such as shear-controlled, orientation injection molding (SCORIM), sequential injection molding and push-pull injection molding have been proposed to eliminate or heal weldlines or both (Bevis *et al.*, 1998; Kühnert *et al.*, 2005; Patcharaphun *et al.*, 2006; Zhou and Mallick, 2006).

Although a thorough search through the literature reveals many references to the weldline strength of thermoplastics and thermoplastic

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composites, little consideration has been given to the weldline strength of rubber-molded parts. Chookaew *et al.* (2010a) investigated the effect of processing parameters on the weldline strength of natural rubber (NR). They found that the clamping pressure and temperature used in the vulcanization process are very important. Previous work by Chookaew *et al.* (2010b) investigated the effect of the filler types and contents on the weldline strength of acrylonitrile butadiene rubber (NBR). They suggested that an increasing amount of calcium carbonate (CaCO_3) had little effect on the weldline strength, whilst with silica (SiO_2), the weldline strength of NBR was much lower than the values obtained for the samples without a weldline. With regard to the effect of thermal aging, they also found that the weldline strength of NBR did not change after an aging test. However, there is still lack of knowledge of weldline strength with regard to the compression molding of NR blends. Furthermore, NR products are being used in a variety of environmental applications such as at high temperature or in hot oil or solvent which may lead to crazing or swelling. These unwanted phenomena may result in a severe reduction in the weldline strength of the NR products. Therefore, in this present study, synthetic rubbers—namely, ethylene propylene diene monomer (EPDM) and acrylonitrile

butadiene rubber (NBR)—were blended into NR in order to enhance the aging properties with respect to the heat, oil and ultraviolet resistance of an NR specimen containing a weldline.

MATERIALS AND METHODS

Preparation of rubber compounds

NR (STR5L) was masticated with EPDM (6505) and NBR (3345) using an internal mixer at a temperature of 70 °C for 5 min. The rubber blends were then mixed with 60 parts per hundred parts (phr) of carbon black (CB330N), commercial grade stearic acid, ZnO and aromatic oil for 10 min so that a homogeneous mixture of the rubber compounds was obtained. An amount of sulfur and accelerator—namely, n-cyclohexyl benzothiazole sulphenamide (CBS) for the NR/EPDM blend and n-tert-butyl-2-benzothiazole sulphenamide (TBBS) for the NR/NBR blend—were added into the rubber compounds on the two-roll mill for about 3 min according to the conventional vulcanizing system (CV), as shown in Tables 1 and 2. Each batch was rolled to produce a sheet approximately 7 mm thick and left at room temperature for 24 hr. Mooney's test was performed to determine the scorch time (t_{scorch}) and viscosity of the compounds using a Mooney viscometer (TECHPRO-visTECH, model

Table 1 Compound formulation of natural rubber (NR) and ethylene propylene diene monomer (EPDM) blends used in this study.

Ingredient	Contents (phr ^a)				
	100	90	70	50	0
NR	100	90	70	50	0
EPDM	0	10	30	50	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
Carbon black	60	60	60	60	60
Aromatic oil	4	4	4	4	4
CBS ^b	1.2	1.2	1.2	1.2	1.2
Sulfur	1.8	1.8	1.8	1.8	1.8

^a phr = Parts per hundred parts of rubber.

^b CBS = n-cyclohexyl benzothiazole sulphenamide

123103). According to the standard test method of ASTM D1646, the test temperature was set at 100 °C and a large rotor was employed. A moving die rheometer (MDR; TECHPRO-rheoTECH, model 121105) was utilized to determine the 90% cure time (t_{90}).

Test piece fabrication

The rubber blends were compression molded (WABASH, 75 t) into sheets approximately 2 mm thick at 150 °C and 45 t (holding pressure time depends on the cure characteristic of rubber compounds). For the sake of comparison, a special compression mold was

designed and constructed (as illustrated in Figure 1) in order to produce the NR/EPDM and NR/NBR specimens with and without a weldline. For the preparation of the specimen without the weldline, the rubber compound was filled either into cavity #1 or cavity #2. In the case of specimens containing a weldline, the same rubber compound was inserted in both cavities. The rubber compound was then compressed by the plunger which was installed on the upper plate (Figure 1). From the vulcanized rubber sheets, dumbbell specimens (Figure 2a) were die-stamped to produce tensile specimens according to the standard tensile test of ASTM D412 (Die C). The thermal, UV and oil

Table 2 Compound formulation of natural rubber (NR) and acrylonitrile butadiene rubber (NBR) blends used in this study.

Ingredient	Contents (phr ^a)				
NR	100	90	70	50	0
NBR	0	10	30	50	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
Carbon black	60	60	60	60	60
Aromatic oil	4	4	4	4	4
TBBS ^b	1.2	1.2	1.2	1.2	1.2
Sulfur	1.8	1.8	1.8	1.8	1.8

^a phr = Parts per hundred parts of rubber.

^b TBBS = n-tert-butyl-2-benzothiazole sulphenamide.

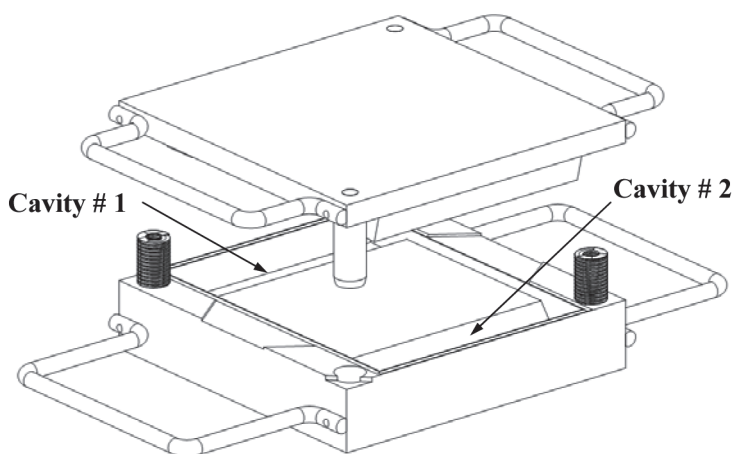


Figure 1 Special compression mold for preparing the test piece.

aging tests were carried out according to ASTM D572, ASTM D4329 and ASTM D417-49, respectively. The weldline strength of the specimens prior to and after the aging test was determined using a universal testing machine (UTM; H50KS, Hounsfield) at a crosshead speed of 500 mm.min⁻¹. The average values of the maximum tensile strength were used for analysis.

RESULTS AND DISCUSSION

Effect of EPDM and NBR contents on tensile strength of NR blends

The effect of blend ratios on the tensile

and weldline strengths of NR/EPDM and NR/NBR blends are illustrated in Figures 3(a) and 3(b). It can be seen that the effect of adding EPDM and NBR did not substantially affect the tensile strength of the NR/EPDM and NR/NBR blends. This appears to contradict the results of previous studies (Botros, 2002; Arayaprane and Rempel, 2007), in which a reduction in the mechanical strength was reported. In the results from the current study, this could probably be attributed to the effect of the high carbon black loading (60 phr) which effectively functions as the reinforcing filler within the EPDM and NBR matrices. It is also clearly evident that the tensile strengths of a

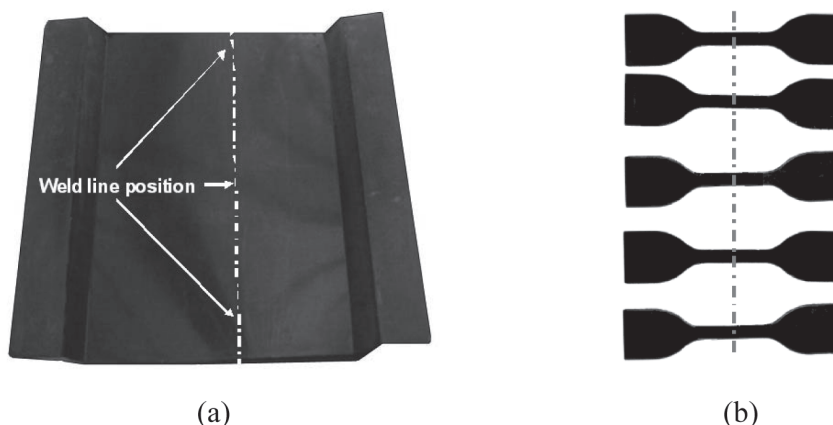


Figure 2 (a) Vulcanized rubber sheet with weldline and (b) Tensile test specimens.

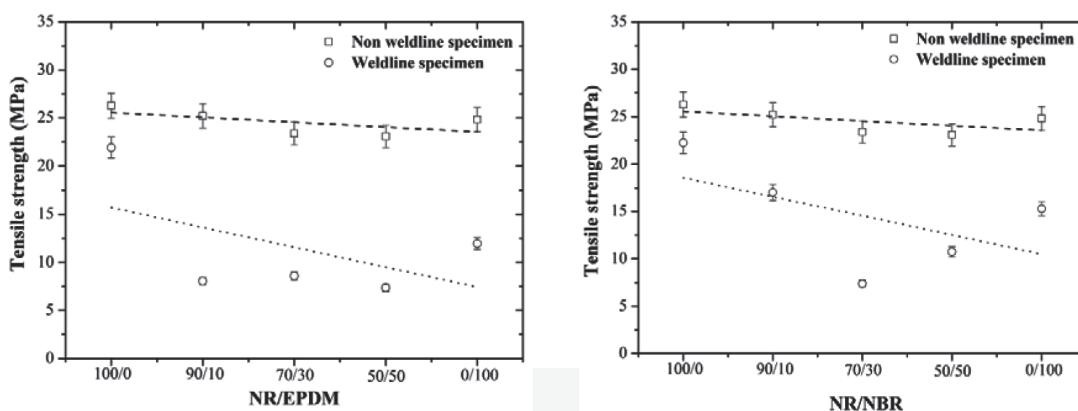


Figure 3 Variation of tensile and weldline strengths for natural rubber (NR) compounded with various ethylene propylene diene monomer (EPDM) and acrylonitrile butadiene rubber (NBR) contents. Vertical bars represent $\pm$ SD.

specimen containing a weldline are much lower than the values obtained from non-weldline specimens. This is not solely due to the reduction of tack properties and the increasing rigidity of the vulcanizates at very high filler loadings which promote crack propagation at the weld interface. In addition, the unfavorable molecular orientation and the existence of a V-notch and microvoids at the weld surface, as presented in previous works by Patcharaphun *et al.* (2005), Chookaew *et al.* (2010a), Chookaew *et al.* (2010b) can also be a source of stress concentration and thus it would be easy to break at this position. Moreover, it should be noted that the weldline strengths of NR blends tend to decrease with an increase in EPDM and NBR loadings. This is possibly due to the different cure characteristic between the rubber compounds. It is well known that NR has a greater number of unsaturated bonds in comparison with EPDM and NBR (Tinker and Jones, 1998) which leads to a more effective use of the sulfur to obtain a satisfactory degree of crosslink, especially at the weld interface.

Effect of EPDM and NBR contents on aging properties of NR blends

Figures 4–6 illustrate the changes in the

weldline strength of NR blends after being subjected to thermal, ultraviolet and oil aging tests. It was clear from Figure 4 that the weldline strength of thermal aging NR vulcanizate (100/0) was much lower than the value obtained from non-aging specimens. The explanation for this is not solely attributed to the remaining double bond and polysulfidic crosslinks that occurred in the CV system, which is strongly prone to reversion at high temperatures resulting in the chain scission of rubber molecules (Blow and Hepburn, 1978; Hofmann, 1989) but also to the increased thermal conductivity and rigidity of vulcanizates with increasing CB contents which promotes heat aging efficiency during the test and crack propagation at the weld interface (Arayaprane and Rempel, 2007; Chookaew *et al.*, 2010c). Considering the UV resistance of NR specimen with weldline (100/0), it is evident that UV aging does not bring about any major changes in the weldline strength of NR. The explanation for this increased stability could be due to the high loading of CB (60 phr), which has a dominant effect on the UV stability of the cured rubber matrix. As can be seen in Figure 6, however, the weldline strengths of oil and hot oil aging NR vulcanizate (100/0) are substantially lower than those of non-aging specimens. The

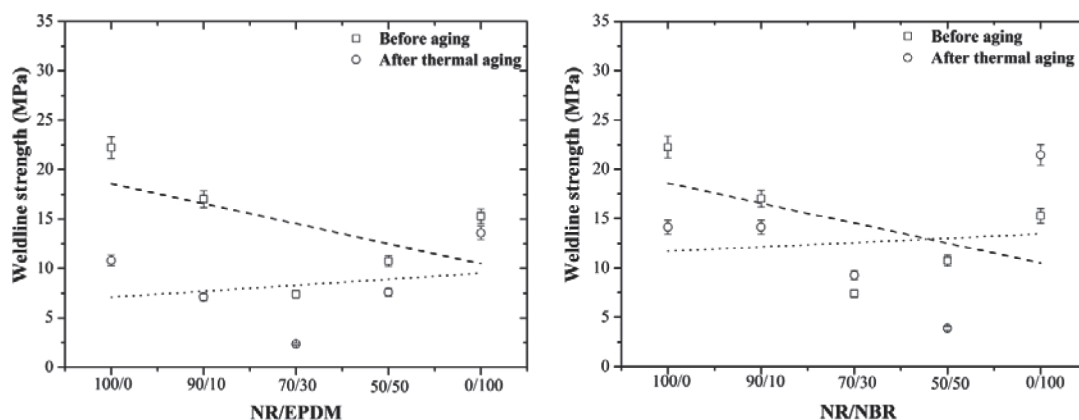


Figure 4 Comparison of weldline strength prior and after heat aging test for natural rubber (NR) compounded with various ethylene propylene diene monomer (EPDM) and acrylonitrile butadiene rubber (NBR) contents. Vertical bars represent $\pm$ SD.

excess amount of sulfur used in this study (CV system) increases the probability of the formation of polysulphide crosslinks resulting in a relative increase in the separation distance between rubber chains. This in turn leads to an increase in penetration of the oil molecules into the rubber matrix, in comparison with those of EV and semi-EV systems, which in turn affects directly on the mechanical strength of the rubber vulcanizates. (Blow and Hepburn, 1978; Hofmann, 1989) The effects of heat on aging have been found to be a

major degrading factor for oxidation in several accelerating tests in that an increased temperature leads to a rapid deterioration. A dramatic drop in the weldline strength of hot oil aging specimens is therefore not solely explained by the higher degree of oil penetration in the rubber matrix but also by the breakdown of the crosslinks (mainly the polysulfidic ones) during the test. The same tendency has also been reported previously (Park *et al.*, 2000). Considering the effect of EPDM loadings on the aging properties of NR containing

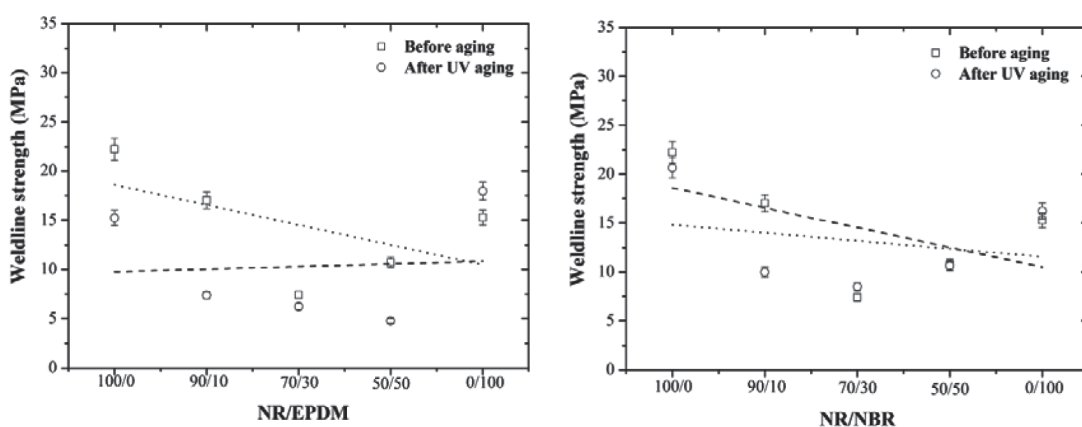


Figure 5 Comparison of weldline strength before and after UV aging test for natural rubber (NR) compounded with various ethylene propylene diene monomer (EPDM) and acrylonitrile butadiene rubber (NBR) contents. Vertical bars represent $\pm$ SD.

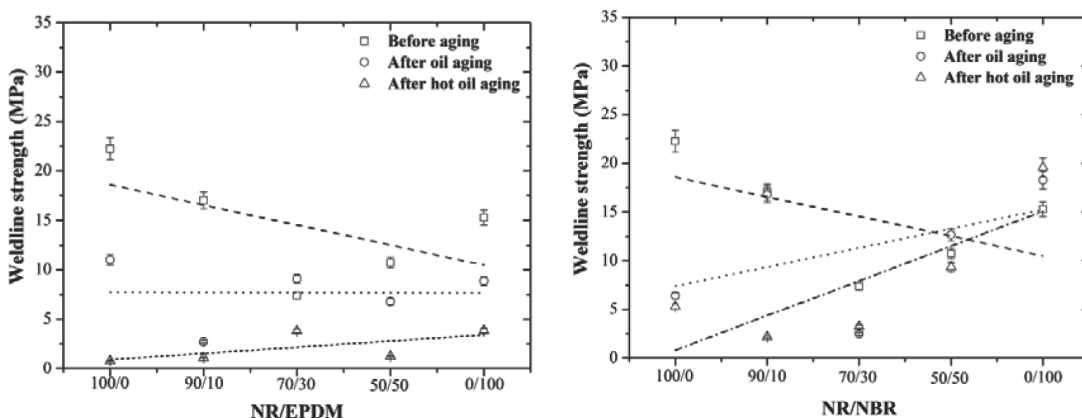


Figure 6 Comparison of weldline strength before and after oil and hot oil aging test for natural rubber (NR) compounded with various ethylene propylene diene monomer (EPDM) and acrylonitrile butadiene rubber (NBR) contents. Vertical bars represent $\pm$ SD.

a weldline, it should be noted that an increased amount of EPDM tends to improve the heat and UV resistances in that the differences between the weldline strengths of aged and unaged specimens become smaller. This is not only due to the fact that EPDM has a saturated and stable backbone structure, as compared to those of NR, but also is due to the post curing reaction of EPDM. As illustrated in Figures 4 and 5, the weldline strengths of EPDM specimens (0/100) after exposure to thermal and UV aging are higher than the unaged ones. However, the weldline strengths of NR/EPDM blends obtained from oil and hot oil aging tests indicated that no substantial improvements of weldline strength were found. This is associated with the non-polar structure of NR and EPDM which can be easily attacked by polar media (such as oils, gasoline and greases) resulting in a high degree of swelling and thus results in a deterioration in the stability of the rubber molecules. In the case of NR/NBR systems, it is clearly evident that the increased amount of NBR improved the aging properties of NR, especially with regard to oil and hot oil resistance. The improved oil resistance of the NR/NBR blends is considered to be caused by the presence of highly polar CN groups in the structure of NBR, while the increased UV resistance is believed due to the very high loading of carbon black (60 phr) which can also enhance mechanical properties as well as act as an excellent UV stabilizer. Furthermore, as presented in Figures 4-6, the weldline strengths of NBR (0/100) after being subjected to thermal and hot oil aging tests were higher than those of unaged specimens. These results also imply that the post curing reaction of NBR occurred during the aging test.

CONCLUSION

In this study, ethylene propylene diene monomer (EPDM) and nitrile rubber (NBR) were blended into natural rubber (NR) specimens

containing a weldline in order to enhance the aging resistance when subjected to heat, ultraviolet light and oil. The results revealed that an increased amount of EPDM tended to improve the heat and UV resistance, while no substantial improvements of oil resistance was found. By considering the effect of NBR loadings on the aging resistance of NR, it was clearly evident that the increased amount of NBR improved the aging resistance of NR, especially for oil and hot oil resistance. This is not solely associated with the high polarity of NBR, but also the post curing reaction of NBR during the aging tests.

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