Autohesion Behavior of Brominated-Isobutylene-Isoprene Gum Nanocomposites with Layered Clay

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총상점토 충전 브롬화 이소부틸-이소프렌 검 나노복합체의 접착거동

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ABSTRACT : The effect of nanoclay (Cloisite 20A) on the self-adhesion behavior of uncured brominated-isobutylene-isoprene rubber (BIIR) has been studied. The dispersion state of nanoclay into the rubber matrix was examined by SEM, TEM and XRD analysis. The thermal degradation behavior of the filled and unfilled samples was examined by TGA and improvement in the thermal stability of the nanocomposites occurred based on the weight loss (%) measurements. Also, addition of nanoclay enhanced the cohesive strength of the material by reinforcement action thereby reducing the degree of molecular diffusion across the interface of butyl rubber. However, the average depth of penetration of the inter-diffused chains was still adequate to form entanglement on either side of the interface, and thus offered greater resistance to peeling, resulting in high tack strength measurements. The improvement in tack strength was only achieved at critical nanoclay loading above 8 phr. Contact angle measurement was also made to examine the surface characteristics. There was no significant interfacial property change by employing the nanoclay.

요약 : 브롬화 이소부틸 이소프렌 (BIIR) 고무의 접착성에 미치는 나노점토(Cloisite 20A)의 영향을 조사하였다. 고무내 나노점토의 분산성은 SEM, TEM, XRD으로 분석하였다. 나노점토 충전 및 미충전 고무의 열적안정성은 TGA로 분석하였으며, 충전고무에서 열적안정성을 보였다. 또한 나노점토를 첨가하면 보강효과에 의해 고무의 강도가 증가하였다. 나노점토 첨가로 계면간 분자확산 정도는 감소할 것으로 판단되었지만, 본 연구에서 관찰된 분자확산에 의해 형성된 계면의 두께는 분자사슬간 얽힘현상을 유발하는데 충분하여 계면접착력이 증가하는 것으로 나타났다. 계면접착력 증가현상은 일정한 이상 (8 phr)의 나노점토가 첨가되었을 때 나타났다. 나노점토 첨가에 따른 표면특성의 변화를 조사하기 위해 접촉각 측정을 하였는데 큰 변화는 관찰되지 않았다.

Keywords : nanocomposites, autohesion, inter-diffusion, brominated-isobutyl-isoprene rubber

I. Introduction

Autohesion is the resistance to separation of two uncured bonded identical elastomer that have been joined together for a period of time under a given temperature and pressure.¹⁻⁵ When two rubber surfaces are joined above their glass transition temperature, distinct macroscopic interface between the joining pieces slowly disappears with time, and the mechanical

strength of the interface progressively increases.

Disappearance of interface is primarily due to the diffusion of polymer chains from both sides across the interface. The most commonly accepted mechanisms for forming adhesive bonds are (i) adsorption, (ii) molecular interdiffusion, (iii) electrostatic interactions, and (iv) mechanical interlocking. Generally, the primary mechanism of autohesion is based on adsorption and interdiffusion. The interdiffusion of polymer chains across a polymer-polymer interface requires the polymers to be mutually soluble and the macromolecules or chain

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Figure 1. Autohesion mechanism in an elastomer, where t_1 is a characteristic time scales of relaxation of rubber molecules.

segment to have sufficient mobility.³ Figure 1 depicts a typical mechanism for autohesion of two elastomers.

It has also been reported earlier that the following conditions must be met by a rubber compound for exhibiting high autohesive tack: (a) two rubber surfaces must come into intimate molecular contact, (b) diffusion of polymer chains across the interface must take place, and (c) bonds formed must be capable of resisting high stress before separation. The first two conditions describe the bond formation and take place in series; i.e., the molecular contact always precedes interdiffusion of chain segments.⁴

Studies on the autohesion can provide fundamental insights into practical engineering issues such as, elastomer tack and polymer fusion etc. This phenomenon has been considered to be one of the most important properties required when building rubber articles from uncured rubber materials. Autohesion (or autohesive tack, self adhesion) plays an important role in the tire industry, where various parts including the impermeable inner lining, the reinforced carcass, and the tread have to hold together until the tire is cured.^{4,5}

Generally, plasticizers like oil facilitate molecular diffusion across the interface by diminishing the entanglement density of the rubber chains, but diluted, interdiffused rubber chains are more easily separated than the neat sample, and hence the tack strength reduces.^{4,6} On the other hand, low molecular weight tackifying resins are added to synthetic elastomer compounds to enhance tack and to prevent tack decay.^{4,6-8} Similar to the action of oil, tackifying resins also reduce the entanglement density of the base elastomer, however, the interdiffused chains diluted with tackifiers resist separation significantly more than those diluted with oil.^{6,8}

It has also been reported that the addition of reinforcing fillers like carbon black can influence the tack strength of elastomers.⁹⁻¹³ For instance, addition of 40 phr of carbon black to natural rubber (NR) resulted in a significant increase in the tack strength of NR.⁹ The increase in the tack strength

has been attributed to an increase in cohesive strength due to filler reinforcement.⁹ On the other hand, addition of carbon black to styrene-butadiene rubber (SBR) resulted in a significant reduction in the tack strength.⁴ Moreover, it has already been established that a typical SBR cannot readily achieve bond formation due to the unfavorable intrinsic characters of the elastomer such as molecular weight and viscosity.¹⁰ The addition of filler further restricts the chain mobility, reducing the interfacial interactions leading to lower tack.¹⁰ Therefore, it was concluded that the effect of carbon black addition on tackification depends more on elastomers' ability to achieve bond formation, rather than its specific chemical nature.^{4,11} Nanoclays have been used as a potential reinforcing agent for various elastomers over the past decade.¹⁴⁻¹⁶ Such nanoclays offer a wide array of property improvements at very low filler loadings, owing to the dispersion of few nanometers thick clay platelets of high aspect ratio.¹⁴ Researchers have extensively studied the effect of different platelet-like montmorillonite (MMT) nanoclays and needle-like sepiolite nanoclays on the physico-mechanical properties of various elastomers.¹⁶⁻²² Most of the early efforts have been focused mainly to understand the influence of these nanoclays on the mechanical, thermal, and physical properties of various elastomers.¹⁴⁻¹⁶ Particularly, the role of nanoclays on modulus, permeability, tear strength and wear behavior of elastomers has also been an important area in the study of autohesion. Controlling these factors will ensure right amount of tackification behavior required to produce rubber articles with good and uniform quality at a constant rate.

In this study, the effect of nanoclay (Cloisite 20A) on the autohesive tack behavior of uncured brominated-isobutylene-isoprene rubber (BIIR) has been investigated with a special regard to (a) nanoclay concentration and (b) morphology of rubber-clay nanocomposites. Bond formation (self-diffusion) and breaking ability (strength of the interface) has been analyzed by studying various distinct tack governing parameters like green strength, 180° peel adhesion test and the tack strength of the nanocomposites. The BIIR was selected due to its appreciable viscoelastic behavior and its wide application in the tire industry as inner liner tubes. Other tests such as stress-strain, X-ray diffraction, transmission electron microscope, thermogravimetric analysis were also carried on the nanocomposites to fully appreciate the dispersion of the nanoclays in relation to the tackification behavior of the filled and unfilled compounds.

II. Experimental

1. Materials and sample preparation

Brominated-isobutylene-isoprene rubber (BIIR) was sup

Table 1. Composition of Mixes Prepared (phr)

Sample Designation	BIIR	Nanoclay (Cloisite 20A)
B	100	0
BC2	100	2
BC4	100	4
BC8	100	8
BC16	100	16

plied by ExxonMobil Chemical, USA. An Organo-modified clay (Cloisite 20A, modified by dimethyl dehydrogenated tallow and quaternary ammonium chloride) was supplied by the Southern Clay Products Inc. Neat rubber (BIIR) was mixed in an internal mixer (B-type Banbury mixer, S. Korea) at 150°C, 60 rpm rotor speed for 3 minutes followed by the addition of Cloisite 20A clay for an additional mixing time of 5 minutes. The mixtures were sheeted out from a two-roll mill (Farrel 8422, USA). A rectangular sheet of samples (150×150×2 mm) were molded by electrical hot press machine (Caver, WMV50H, USA), at a pressure of 1.1GPa for 5 minutes and at 100°C temperature. Samples were pressed in-between a Mylar™ film sheet of ≥ 1 mm thickness fabric. They were then left for overnight and strips of 150×15×2 mm sizes were cut out for the peel test. Samples were also prepared in the same procedure and standard dumbbell shapes were cut out for the green strength test. However, in this case pressing of the sample was done in-between two aluminum foils. Table 1 depicts the sample formulation and designations.

2. Characterization

2.1. Tensile strength measurement

The tensile strength measurement was carried out according to ASTM D412 standard by using (LLOYD instrument, UK). Prior to the test, the aluminum foils covering the faces of the dumbbell-shaped specimens were removed and then subjected to stress-strain test at a cross-head speed of 500 mm/min and 25°C temperature. The maximum tensile stress was taken as the green strength from the generated stress-strain curve and at least four samples were tested for each composition and averaged.

2.2. Tack strength measurement

The tack strengths of the samples were also examined. In this case, the Mylar™ films were removed from the surface of the two strips, and two surfaces were gently brought together. A pressure system of about 0.13 MPa was applied gently and uniformly on each side of the bonded strips with an area of surface contact of 15 mm², at equal rate. At least

Figure 2. A photo of autohesive tack measurement by 180° peel test geometry.

each press lasted for a contact time of about 5 s (10 s in all for the two sides). The slightly given pressure at the short chosen time was to ensure inter-diffusion and the removal of entrapped air bubbles at the interface of the bonded strips. Immediately after the contact time was reached upon pressing, sample was removed immediately and subjected to the peel test using the tensile tester. The peeling test was based on 180° orientation (T-type peeling test) and at a speed of 100 mm/min. The testing machine generates a plots of the force (N) required to separate the bonded strips against the distance of separation (mm). A typical illustration of sample under 180° orientation peeling at a peeling speed of 100 mm/min is shown in Figure 2. The average forces required for separating bonded strips were recorded and together with the samples width, the tack strength G_a (N/m) was calculated using the equation below:

$$G_a = \frac{2F}{w} \quad (1)$$

where F is the estimated average peel force (N) and w is the width of the strips of the samples. For each composition, four samples were tested, and averaged.

2.3. Wide angle X-ray diffraction (WAXD)

To investigate the d-spacing of dispersed clay platelets, WAXD studies was conducted using PANalytical X-PERT Powder diffractometer, (Netherland) in the range of $2\sim 10^\circ$ with Cu-K α radiation ($\lambda = 0.154$ nm). The X-ray diffraction patterns were obtained at room temperature based on a continuous scan steps. The d-spacing was calculated using the Bragg's equation. The samples were placed vertical in front of the X-ray source. The detector was moving at an angle of 2θ while the sample was moving at an angle of θ .

2.4. Scanning electron microscopy (SEM)

Cryogenic fracture surfaces of uncured BIIR-nanoclay samples were sputter coated with platinum metal and different portion of the fractured surfaces were observed with a scanning electron microscopy machine (JEOL, JSM 599, Japan), at room temperature.

2.5. Transmission electron microscopy (TEM)

Ultrathin representative specimen (thinner than 100 nm) for TEM observation were cryogenically cut with a diamond knife using ultramicrotome (Leica Ultracut CUT, Germany) and collected on 200-mesh copper grids. The dispersion of the cloisite nanoclays in the BIIR matrix was observed with TEM (JEOL, JEM 2100, Japan).

2.6. Contact angle measurement

The contact angle of representative samples were determined using a contact angle meter (Tantec half angle technique, US Patent, #5,268,733 CAM-PLUS MICRO X12 110V). Water was used as a polar liquid. Strips of samples with dimensions of $10\times 10\times 1$ mm were cut from molded sheet-like samples and subjected to the test. A 10 μ m pipette was used to collect the liquids and gently dropped onto the surface of the sample. Reading was done 1 min (for that was the period

suitable for the test) after dropping the liquid onto the sample's surface. Four samples were tested for each composition and averaged.

2.7. Thermogravimetric analysis (TGA)

TGA Q50 mode (TA Instrument, US/TA5000/TGA 2050), was used to investigate the thermal degradation behavior of the BIIR-nanoclay composite. The conditions include a nitrogen medium with a equilibrium temperature of 25°C at a heating rate of $10^\circ\text{C}/\text{min}$ to 700°C .

III. Results and discussion

1. Morphology and dispersion of nanoclay

The X-ray diffractograms of the pristine Cloisite 20A nano clay and BIIR-Clay nanocomposites are shown in Figure 3.

Figure 3. X-ray diffractograms of the pristine Cloisite 20A clay and BIIR-Cloisite 20A nanocomposites: B, BC4 and BC16.

Figure 4. SEM micrograph of representative samples: (a) B and (b) BC16.

Figure 5. TEM micrographs of representative samples: (a) BC2 and (b) BC4.

From the X-ray diffractogram of the pristine clay the basal characteristic peak (001) for Cloisite 20A appears to be at $2\theta = 7.2^\circ$ ($d_{001}=1.23$ nm). For the binary nanocomposites of BIIR-cloisite clay, this peak shifted to lower angles around $2\theta = 5.5^\circ$ suggesting an increase of the d-spacing of the galleries of the organoclay. The d-spacing of the nanocomposite was higher than the virgin organoclay. Moreover these peaks were broad and this signifies an intense intercalation of polymer chains inside the clay layers (see Figure 3).

The SEM micrographs of fractured uncured neat rubber B and a representative of an uncured binary nanocomposite are shown in Figure 4. From the SEM micrograph, it can be seen that the neat BIIR phase is smoother on the surface and regular in shape with less number of troughs as compared with the nanocomposite. Yet, some tiny whitish spots which could be an evidence of the presence of nanoclays were observed on the surfaces of the highly filled nanocomposite (see Figure 4b). Since signs of agglomerates present were unusable with this kind of test, as such TEM analysis was adopted to confirm such tendencies.

In order to be certain of successful nanoclay dispersion within the bulk butyl rubber, TEM analysis was carried on the samples and the results (micrograph) is shown in Figure 5. In the case of BIIR-clay nanocomposites, a coarse morphology with tactoids of various sizes is observed which corresponds to intercalation of polymer chains within the clay galleries. This agrees well with the WAXD results. Even though, the TEM micrographs of the filled samples confirmed successful dispersion of nanoclay within the rubber matrix, an evidence of bulk clay agglomerates was observed (indicated as dark spot in the TEM images). It must be noted that these agglomerated regions were common among the specimens with higher nanoclay loading. A typical example is as shown in Figure 5b.

2. Effect of nanoclay on the green strength of BIIR-clay nanocomposite

Figure 6 presents stress-strain (σ - ϵ) curves of the filled and unfilled butyl rubber. It was observed that the addition of nanoclays stiffened and also improved the strength of the rubber. The tensile properties (50% modulus, elongation at break and maximum tensile stress) have been presented in Table 2. The increase in the strength and elastic modulus of BIIR explains the reinforcing action of nanoclay. Noticeably, addition of the nanoclays increased the area under the σ - ϵ curve by concurrently increasing the maximum tensile stress of the highly filled rubbers, at high strain levels. For instance, the maximum tensile stress and the modulus at 50% of the sample BC16 was approximately 28% and 63% higher than that of the neat

Figure 6. Tensile stress vs. strain of representative samples.

Table 2. Tensile Properties of Unfilled- and Filled-Butyl Rubber

Specimen	B	BC4	BC8	BC16
Maximum Tensile Strength (KPa)	304	314	327	389
Modulus (KPa)	134	151	157	219
Elongation at break (%)	≥ 2000	≥ 2000	≥ 2000	≥ 2000

butyl rubber. This suggests the potential of the highly filled rubbers especially BC16, to dissipate a greater amount of energy before failure as compared to sample B.

However, if indeed the green strength of the filled rubbers were improved by the reinforcement action of the nanoclays, then one could speculate a similar tendency in the case of the autohesive tack strength behavior of the respective rubber nanocomposites, as compared to the neat rubber.

3. Effect of nanoclay on the tack strength of BIIR-clay nanocomposite

The variation of peel force plotted against distance of separation of representative samples are shown in Figure 7(a). As can be seen, a trend of fluctuation along the interfacial plane of the bonded strips occurred during the peeling period. This could be due to roughness of the interface topography caused by adsorbed fillers or entrapped air bubbles. It is worthy to state here that, minimal fluctuations were observed in the case of the neat rubber, since its surface seemed much smoother. Despite these variations that were encountered, peeling occurred along the interface over a sufficient distance which enabled estimation of the average peel force for computation of the of tack strengths, G_a (N/m) of specimen.

Three transition behaviors were observed in the study of the autohesive tack properties of butyl rubber filled with cloisite 20A. The tack strength of butyl rubber at different clay concentration has been shown in Figure 7(b). In the first transition, butyl rubber initially showed dramatic tack strength above 1.3 N/m than the samples loaded from 2–8 phr. This indicated that butyl rubber has inherent good tackification properties. This seemed lucid because, according to Bussemaker,²³ it is well known that a freshly cut rubber surface give highest tack. However, in the second transition, it was fascinating to find out that, adding a clay content of 2 phr to the neat rubber caused a drastic drop in the tack strength of the neat rubber (sample B). The third transition involved a gradual increase in the tack strength of butyl rubber with clay content of 2–16 phr. The prominent event here was that, even in the case of this steady growth, the tack strength of the neat butyl rubber was still higher than the samples loaded with 2–8phr nanoclays. Significant improvement in the tack strength of the rubber only

Figure 7(a). Peel force vs. distance curves for representative samples: B, BC2, and BC16.

Figure 7(b). Tack strength of BIIR-cloisite 20A nanocomposites as a function of clay loading.

occurred above 8phr clay concentration. This is not surprising because it is generally known that, unaged butyl rubber is gummy with relatively broad molecular weight and high viscosity behavior.²⁴ As such, with these noted properties, the BIIR stand the tendency of showing good autohesion behavior even without the nanoclays addition. In a recent study by Kumar

Figure 7(c). Autohesive tack strength of selected joint systems: B (between B-B strip), B-BC16 (between B-BC strip), and BC16 (between B16-B16).

et al.⁸ on the autohesion behavior of BIMS filled with needle-like sepiolite nanoclay, they obtained 1 KN/m tack strength for the neat BIMS rubber with optimum contact time of 15 s and pressing load of ~20 N. In the case of this current study, more than 1.3 KN/m tack strength was recorded for the neat BIIR at a chosen contact time of 10 s at pressing load of ~19 N. This could justify one reason why BIIR is a rubber with good inherent self-addition properties, especially as compared to BIMS.

The initial reduction of the tack strength of BIIR upon addition of the clay content (2-8 phr) could draw an attention that only a critical amount of nanoclay content (> 8 phr) was necessary (in our case) to enhance the tack strength of butyl rubber enormously. This reduction could simply suggest that, the nanoclay addition may have either destructed the inherent interfacial flow behavior of the original neat butyl rubber (B) or the reinforcement action was significantly not enough to elevate the tack strength of butyl rubber, especially at these lower amounts of clay loadings. Meanwhile, other literatures have also reported that addition of carbon black to SBR and EPDM lowers the tack strength as compared to that of the gum elastomers.^{4,10,11,25,26}

On the contrary, adding nanoclay content above 8 phr, sufficiently improved the green strength of the specimen without the material losing its original interdiffusion or contact flow properties fully. According to Kumar et al.,⁸ it is well-known that the addition of reinforcing fillers will increase the green strength of synthetic elastomers and can reduce the contact flow and extent of diffusing rubber molecules at the tack junction. If the reduction in contact flow dominates over the enhancement in green strength, there will be reduction in the tack strength. It was stated that, that addition of fillers, espe-

cially active fillers, is beneficial to tack strength.²³ One would suppose that the surface available for intermolecular contact is decreased by filler particles. However, this seems to be more than compensated for by improvement in green strength of the compound, and perhaps by formation of bound rubber around the particles. Therefore, it can be established that the effective interdiffusion and the development in the green strength as a result of reinforcement action, accounted for the improvement in the tack strength of the filled rubber especially above 8 phr. As stated earlier, the contact flow of the bonded specimens reduced due to restricted chain mobility by incorporating the nanoclays into the rubber. Despite these chain mobility constraints, the minimum interdiffusion that occurred within the allowed contact time for the filled samples was still enough to establish effective interdiffusion and chain entanglements across the interface and thus, resulted in higher tack strength measurements.

Furthermore, in this study, we also noted that, increasing the nanoclays concentration in the bulk rubber made the nanocomposite much stiffer (by physical examination) compared to the specimens with lower loadings or the unfilled rubber. This stiffening effect introduced an additional bending strength that was essential to be compensated during the peeling test. It is therefore reasonable enough to assume that, the higher tack strength values obtained for the filled rubbers may be due to the synergy effect of the effectiveness of the interdiffusion, the green strength and the bending force introduced.

In order to demonstrate the role of the interfacial contact played, the autohesive tack strength of B-BC16 (joint strength between a strip of B and another strip of BC16) was analyzed and compared with individual B and BC16 sample. It was exciting to notice that the tack strength of sample BC16-BC16 was still higher than of B-BC16 (joint strength between a strip of B and another strip of BC16) or the B-B (joint strength between a strip of B and a strip of B) sample. The lower tack strength of B-BC16 sample could be attributed to interfacial non-uniformity of the joint specimen (B and BC16). At microscopic level, specimen BC16 would show a much stiffness and rougher surface topography (with restricted chain mobility), due to the high concentration of the nanoclays compared to the neat rubber B. These two strips in contact under a slight load may still fall short of effective contact flow. The interface may also contain much entrapped air bubbles due to interfacial coarseness introduced by the counterpart specimen (BC16), even after the load application. Further the sample B is associated with lower green strength since it is unfilled. Such conditions could be the result of the lower tack strength measured for the specimen B-BC16.

The contact angle measurements of the unfilled and clay loaded sample has been analyzed to further assess the role of the interface in autohesive tack strength behavior of butyl

Table 3. Contact Angle of Water at 25°C

Samples	Contact Angle (θ°)
B	95 ± 0.4
BC2	94 ± 4
BC4	94 ± 2
BC8	92 ± 0.4
BC16	91 ± 1

Figure 8. TGA and DTG thermograms of butyl rubber and its nanocomposites with clays.

rubber filled with nanoclays. The results obtained (shown in Table 3) suggest that, the addition of Cloisite 20A nanoclay does not alter the surface properties of the neat BIIR rubber much. It was only noticed that, increasing the clay concentration fairly improved the hydrophilicity of BIIR-nanocomposites associated with good wetting properties. Besides, it was observed that most of the surface regions of the nanocomposites still remained uncovered rubber molecules, which supported interfacial molecular diffusion and subsequently

bond formation.

Similar to our previous studies,²⁷ self-adhesion behavior of elastomers coated with carbon black was examined. Despite the several attempts to cover the surface of the elastomers by multiple coatings with the carbon black layers, a fraction of the elastomer interface still remained rubbery for self-adhesion to occur. It can therefore be established here that, nanoclay addition to the rubber did not influence the surface chemistry much, as most of the rubber surface remained rubbery which in turn prompted self-diffusion and consequently improved the autohesive tack behavior of the butyl rubber.

4. Thermal degradation behavior of BIIR-clay nanocomposites

The thermal degradation behavior of pristine butyl rubber and its binary nanocomposites with different loadings of organoclay are depicted in Figure 8. The temperature corresponding to the 5 wt% loss was taken as the initial degradation temperature (T_{onset}) and the temperature corresponding to the maximum value (peak) in derivative thermogram (DTG) was considered as temperature for maximum degradation (T_{max}).

As evident from the Figure 8, butyl rubber started to degrade at around 318°C and the peak maxima of the DTG curve which gave the temperature of maximum degradation (T_{max}), appeared at 405°C. Yet, no much difference in the values of onset degradation temperature (T_{onset}) and temperature for maximum decomposition (T_{max}) of sample B, BC2, BC4 and BC8 was seen. By characterizing the thermal behavior of the specimen based on the weight loss obtained from the TGA, it was seen that, the weight loss of the rubber improved by incorporation of the nanoclays, with BC16 recording the least weight loss value (see Table 4).

The reduction in weight loss as a result of the nanoclay addition could be used as a clear evident of thermal stability enhancement of the nanocomposite, relative to the neat rubber. The improvement in thermal stability of the nanocomposites can be attributed to the fact that, the nanoclay forms a protective layer on the surface of the matrix, which in turn inhibited oxidation processes. Apparently, in case of BIIR/Cloisite 20A nanocomposites, one distinct degradation peak pattern was observed;

Table 4. TGA Data of Investigated Samples

Composition	T_{onset} (°C)	T_{max} (°C)	Residue (%)	Weight Loss (%)
B	318	405	1.32	98.7
BC2	312	407	2.9	97.1
BC4	308	405	4.6	95.4
BC8	307	405	6	94
BC16	304	429	9.7	90.3

the T_{onset} slightly shifted to lower temperatures while T_{max} slightly shifted to higher temperatures.

IV. Conclusions

The effect of organoclay (Cloisite 20A) on the autohesive tack (self-adhesion) behavior of brominated-isobutylene-isoprene (BIIR) rubber has been investigated. Even though, morphological study by SEM did not show any remarkable features of the nanoclay scattering, yet successful dispersion of the nanoclays was confirmed by the TEM and XRD analysis. For example the XRD spectrum revealed an intense intercalation of the polymer chains within the interlayer spacing of the nanoclays. Despite this, evidence of some agglomerated regions was observed and this was common among the samples with the high clay concentration.

It was confirmed that the tack strength of butyl rubber improved substantially only above a critical clay loading level of 8 phr, with BC16 showing extreme tack strength. Although several properties such as discussed earlier could influence autohesion behavior of an elastomer, nevertheless, we found out that the synergy effect of the effectiveness of the interdiffusion, the green strength and the compensated bending strength was perhaps the result of the intense boost in the autohesive tack strength of the rubber.

It was clear from the contact angle measurement that most of the surface region of the clay loaded samples still remained rubbery that promoted interdiffusion and facial bond formation. Moreover, the addition of the nanoclays to the butyl rubber gradually improved the thermal stability of the nanocomposites by forming protective layers in the rubber matrix which delayed the degradation of bulk composite. The results and the findings obtained could provide some useful information for future research on self-adhesion behavior of rubber-clay nanocomposites.

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