ผลของสมบัติต่างๆในและสมบัติที่พื้นผิวที่มีต่อสมบัติการติดของยาง

Effect of bulk and surface properties on adhesion of rubbers

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บทคัดย่อ

วัตถุประสงค์ของงานวิจัยนี้ เพื่อศึกษาถึงผลของสมบัติภายในและสมบัติที่พื้นผิวของยางที่มีต่อสมบัติการติดของยาง หมายถึง การติดกันระหว่างยางกับแก้ว และสมบัติการติดด้วยตนเองของยาง หมายถึง การติดกันระหว่างยางกับยาง ยางธรรมชาติ (NR) ที่ได้เตรียมมาจากน้ำยาง Hevea สำหรับยางผสมชนิดที่เข้ากันไม่ได้ เช่น ยางpolyisoprene (IR) และ ยางไฮโดรจิเนเตด acrylonitrile但adiene (HNBR) ถูกเตรียมขึ้นโดยใช้เครื่องบดผสมระบบปิด โดยตัวอย่างยางที่เตรียมจากถูกทำให้สุกหรือคงรูปได้โดยการฉายแสงอย่างเต็มตัวของที่ความเข้มแสงต่างๆ ในการศึกษาสมบัติการติดและสมบัติการติดด้วยตนเองของตัวอย่างยางได้ใช้เครื่องมือทดสอบที่ถูกพัฒนาขึ้นมาของชนิดคือ (1) โดยการกระแทกของแท่งเพนดูลัม (pendulum) ที่เวลาในการสัมผัสช่วงสั้นๆ เป็นมิลลิวินาที่ และ (2) โดยการสัมผัสของแท่งโพล hospitalized (probe) ที่เวลาในการสัมผัสนานขึ้นเป็นชั่วโมง พบว่าสมบัติการติดและสมบัติการติดด้วยตนเองของตัวอย่างยางทั้งหมดเพิ่มขึ้นตามเวลาที่ใช้ในการสัมผัส ส่วนสมบัติเชิงกลในการเคลื่อนที่แพร่ผ่านของสายโซมolecular ถูกนำมาอธิบายเฉพาะในกรณีของยางสุก นอกจากนี้ยังพบว่า พลังงานการติดของยางผสมระหว่างยาง IR และยาง HNBR เพิ่มขึ้นตามปริมาณของยาง IR ที่เวลาในการสัมผัสโดยๆ

ABSTRACT

The objective of this study is to investigate the effect of bulk and surface properties of rubbers on both their adhesive properties as rubber/glass contact and their self-adhesive properties as rubber/rubber contact. A natural rubber (NR) was prepared from Hevea latex. Blends of immiscible rubbers, i.e. synthetic polyisoprene rubber (IR) and hydrogenated acrylonitrile butadiene rubber (HNBR) were prepared by means of an internal mixer. All rubbers were crosslinked by electron beam irradiation at different doses. Two experimental devices are specially devoted to measure the level of adhesion and self-adhesion: (1) by impact of a pendulum at very short contact times in milliseconds and (2) by contact of a probe for longer contact times in hours. It appears that adhesion and self-adhesion of all the rubbers increase with contact time. Molecular dynamic of the interdiffusion of macromolecular chains is particularly analyzed in the case of crosslinked rubbers. Moreover, the adhesion energy concerning rubber blends of IR and HNBR increases gradually with IR content for a given contact time.

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INTRODUCTION

Adhesion phenomena are of great importance in many scientific and technical fields, many applications of polymers rely on their adhesion, between chemically different polymers or between a polymer and a non-polymer, and on their self-adhesion, between two identical polymers. It is the case in particular for rubbers. Rubbers are frequently used as matrix in composite materials, for example tires, belts and coated fabrics, or in contact with other solids. The production and the use of rubber based materials are developed in many industries, such as tire application, athletics, textiles, stationery, until aerospace, etc. The adhesive substances may be natural or synthetic. The characteristics of the products used within this framework are adjusted in order to control adhesion, in other words, the energy level which it is necessary to separate two materials in contact. Therefore, adhesion or tack is an important property for most of practical uses of rubbers.

Tack is defined as the energy required to separate two materials put into contact for a short time under a light pressure (Smithipong et al., 2004). We can distinguish between adhesive tack or adhesion, when materials in contact are different and self-adhesive tack or self-adhesion, when both materials are identical. To obtain high values of tack, an intimate molecular contact must be first established between the two surfaces. Such an intimate contact is a necessary condition so that specific interactions, in addition to Van der Waals interactions, take place at the interface. In particular, interdiffusions of macromolecular segments across the interface in the case of elastomer/elastomer contact. Since tack is evaluated by the energy required to propagate an interfacial fracture, it strongly depends on the interfacial adhesive strength but also on the energy dissipated in polymer during separation, through viscoelastic losses, fibrillation phenomena, etc. It is generally observed that tack is dependent on surface roughness and increases with contact time, contact force and separation rate (Zosel, 1998; David et al., 2000).

The objective of this study is to investigate the effect of bulk and surface properties of uncrosslinked rubber, crosslinked rubber and rubber blends on both their adhesive properties as rubber/glass contact and their self-adhesive properties as rubber/rubber contact.

MATERIALS AND METHODS

Materials: Natural rubber (NR) was prepared from Hevea latex. Synthetic polyisoprene rubber (IR), Natsyn 2200 from Goodyear Tire and Rubber Company, was also used as a reference material. Blends of immiscible rubbers, i.e. IR and hydrogenated acrylonitrile butadiene rubber (HNBR), Therban® A 3907 from Bayer AG, were prepared by means of an internal mixer. Certain rubbers were crosslinked by electron beam irradiation at different doses. This irradiation process presents the main advantage to be performed quickly and at room temperature. Final products exhibit similar characteristics as those obtained by chemical procedures like sulphur or peroxides. Moreover, no
chemical crosslinking agents near the rubber surface have to be considered. This is very important for adhesion science.

Two different silica glasses were chosen as substrates: a glass plate of 25 mm diameter, glass A, for the pendulum test and a glass rod of 5 mm diameter, glass B, for the probe test. Glass surfaces were cleaned in an ultrasonic bath with toluene and acetone for about 5 min in each solvent and 5 min in a 1% aqueous solution of sodium hydroxide. They were rinsed with double-distilled and deionized water and dried under nitrogen flow.

Adhesion and self-adhesion test methods:

Two experimental devices were specially developed to measure the level of adhesion and self-adhesion (Gent et al., 1990, Creton et al., 2001). For very short contact times from a few milliseconds up to 0.1 second, a plane/plane contact was obtained by impact of a pendulum (Figure 1a). Various contact times from 3 to 70 ms were obtained by adjusting the stiffness of the spring supporting the impacted substrates: these experimental values of contact times are in good agreement with theoretical estimations. They seem to be independent of the impact speed, the nature of the clean and talc powdered surfaces and the nature of the samples. The impact speed can be varied between 40 and 80 cm/s for a pendulum of 500 g. Tack energy was obtained from the difference of kinetic energies between both impacts by using equation (1):

$$ G = \frac{m(V_p^2 - V_c^2)}{2A} \quad (1) $$

where \( G \) is the tack energy per unit interfacial area, \( m \) is the pendulum mass, \( V_p \) is the rebound velocity for the powdered samples, \( V_c \) is the rebound velocity for the clean samples and \( A \) is the contact area.

The second device is a contact probe test using a tensile testing machine (Lhomargy DY-34, Figure 1b), which allows us to evaluate tack at longer contact times, i.e. from 0.1 second to a few hours. With this device, it was possible to record simultaneously and precisely the force, the displacement and the contact area as a function of time during the experiment. All the parameters were carefully controlled, such as rates of contact (10 mm/min) and separation from 1 to 50 mm/min, contact time from 0.1 to 10,000 s, as well as compressive displacement (0.1 mm). The contact area was determined with a high speed camera by means of a mirror and side-views of the interfacial phenomena could be obtained with a second camera. The total energy required for the separation of the two surfaces in contact was obtained by integration of positive values of the force as a function of displacement. However, to compare the different samples, tack energy has to be expressed per unit area, according to:

$$ G = \frac{1}{A} \int F(x)dx \quad (2) $$
where \( G \) is the tack energy \((\text{J/m}^2)\), \( F \) the measured force, \( x \) the displacement and \( A \) the contact area before separation.

**Figure 1**: Tack or adhesion measurements, (a) pendulum test for very short contact time; (b) probe test for longer contact times.

**RESULTS AND DISCUSSION**

1. **Material characterization**

   All samples were first characterized by many techniques: FTIR and Raman spectrometry, DSC, GPC, etc. The physical properties of all uncrosslinked rubbers and glasses are presented in Table 1 (Smitthipong et al., 2004). In the case of crosslinked rubber, an increase in crosslinking efficiency with the irradiation dose is observed, this increase being much more pronounced for HNBR. It appears that the molar mass between crosslinks \( M_c \) for NR and IR irradiated networks are higher than these generally obtained when peroxide crosslinking agents as dicumyl peroxide are used (Figure 2). This means that weakly crosslinked rubbers could be obtained by electron beam irradiation. The master curve for crosslinked rubber relating its elastic modulus to a reduced frequency and obtained by applying the well-known principle of time-temperature superposition is studied. There is also no significant difference between master curves corresponding to uncrosslinked and weakly crosslinked rubbers in each case (Smitthipong et al., 2007a).

   In the case of immiscible rubber blends between IR and HNBR, the morphology of the blends indicates a two-phase structure in which one component is dispersed as domains in the other continuous matrix. IR is dispersed in continuous matrix HNBR as long as the IR contents do not exceed 30% wt. Beyond this concentration, there is a phase inversion and it is the IR phase which becomes the continuous phase. Figure 3 shows that on the surface of the blends between 50% IR and 50% HNBR, HNBR particles disperse in an IR continuum (major phase). Then, a three dimensional structure of the blends can be built and identified by Raman spectrometry. Results found by Raman spectroscopy were in good agreement with those obtained by Scanning Electron Microscope (Smitthipong et al., 2007b).
Table 1: Physical properties of different uncrosslinked rubbers and glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (g/mol) $\times 10^{-5}$</th>
<th>$M_n$ (g/mol) $\times 10^{-5}$</th>
<th>Gel content (% wt/wt)</th>
<th>$T_g$ (°C)</th>
<th>$\gamma_d$ (mJ/m$^2$)</th>
<th>$\gamma_p$ (mJ/m$^2$)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>5.41</td>
<td>2.29</td>
<td>22.5 ± 4.7</td>
<td>-66</td>
<td>29</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>3.72</td>
<td>2.16</td>
<td>0.7 ± 0.2</td>
<td>-65</td>
<td>30</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>HNBR</td>
<td>1.01</td>
<td>0.42</td>
<td>12.3 ± 2.1</td>
<td>-23</td>
<td>33</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Glass A</td>
<td>20</td>
<td>46</td>
<td>20</td>
<td>46</td>
<td>2.0 ± 0.1</td>
<td></td>
<td>231.4 ± 3.5</td>
</tr>
<tr>
<td>Glass B</td>
<td>24</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: $M_w$ and $M_n$ were determined by GPC. Glass transition temperature ($T_g$) was determined by DSC. $\gamma_d$ and $\gamma_p$ are the dispersive and polar components of surface energies, respectively. The surface energies of materials were determined by contact angle measurements. Roughness of glasses was determined by AFM.

Figure 2: Evolution of the molar mass between crosslinks ($M_c$) as a function of the soluble fraction for crosslinked IR by electron beam irradiation and peroxide agent, dicumyl peroxide or DCP.

Figure 3: Spectra (left) and scanning image (right) of Raman spectrometry of the blends between 50% IR and 50% HNBR at the interface.
2. Adhesion and self-adhesion energies

Adhesion and self-adhesion of various rubbers and rubber blends were studied by means of the two types of test, pendulum and tensile testing machine, described following. Adhesion energies for rubber/glass contact of the various systems increase with the separation rate in good agreement with the rheological model of adhesion (Gent et al., 1972), this increase depending on the mechanical and rheological properties of rubbers.

Adhesion and self-adhesion energies of rubbers, crosslinked or not, and rubber blends, increase considerably with the contact time. This is attributed mainly to the rearrangement of the interfacial zone in the case of adhesion against glass and to interdiffusion of macromolecular chains across the interface for rubber/rubber junctions (Tirrell, 1984; de Gennes, 1989). Self-adhesion energy, in all cases, is higher than adhesion energy whatever the contact time, indicating that extraction or breaking of interdiffused chains or segments at the interfaces increases the energy required the propagate the fracture, even at short contact times (Figure 4) (Smithipong et al., 2004).

![Diagram](image_url)

**Figure 4:** Variation of adhesion and self-adhesion energies versus contact time of uncrosslinked rubber for two types of tests.

In the case of crosslinked rubbers, adhesion and self-adhesion energies increase with the molar mass between crosslinks ($M_c$) in logarithmic scales, in good agreement with the recent developments in molecular dynamics (Figure 5a) (Vallat et al., 1991). Finally, for the rubber blends between IR and HNBR, adhesion energy increases with the IR content in the blends at a given contact time, without following a simple law of mixing. Self-adhesion energy of the blends in contact...
with raw IR strongly increases with the IR content and is very largely higher than a linear variation (simple law of mixing). On the other hand, the self-adhesion energy of these same compositions in contact with raw HNBR decreases with their IR content and is weaker than a linear variation (Figure 5b). The whole of these results would confirm the existence of an excess of IR concentration on the surface of the blends, whatever the composition of the latter, in good agreement with previous observations, by Raman spectroscopy. This variation translates the influence of the surface morphology on the blend compositions.

Figure 5: (a) Adhesion energy for crosslinked rubber/glass as a function of molar mass between crosslinks ($M_c$) for the probe test. (b) Evolution of self-adhesion energy for rubber/rubber of rubber blends as a function of IR content in HNBR and as a function of contact nature: rubber blends in contact with raw IR or raw HNBR (probe test).

Adhesion between IR and HNBR, immiscible rubbers, is weaker than self-adhesion of one or other pure rubber, indicating that interdiffusion of macromolecular chains at the interface plays a major role in this field. This interdiffusion is necessary to obtain a high level of self-adhesion (Jud et al., 1981).

**CONCLUSION**

All the uncrosslinked or crosslinked rubber and rubber blends were firstly characterized by several techniques. The pendulum test and the probe test were specially used to determine the different levels of adhesion and self-adhesion energies $G$ of the rubbers for a very broad range of contact times from a few ms to a few hrs. Both types of energies increase with contact time due to interfacial rearrangement (adhesion) and macromolecular chains interdiffusion (self-adhesion) across the interface. The effect of molecular dynamics on interdiffusion phenomena is particularly analyzed in the case of crosslinked rubbers. Finally, the adhesion energy concerning rubber blends of IR and HNBR increases gradually with IR content for a given contact time, without following a simple law of mixtures.
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