Thermogravimetric and Swelling Studies on the Natural Rubber Based Super Elastomer

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ABSTRACT

The Thermal stability and solvent transport properties of elastomeric blends of natural rubber and exudated resin of Ailanthus Malabaricum tree were studied in detail. The elastomeric blend samples have been prepared from solution casting technique. Benzene was used as a common solvent for both the constituent polymers to prepare the blends. The resulting material exhibits excellent elastic properties. Thermogravimetry was employed to analyze the thermal stability of natural rubber by the addition of resin. The temperatures at various weight losses for different samples were determined from Thermogravimetric curves. The activation energy of degradation was calculated from Horowitz Metzger equation. The addition of natural rubber improves the thermal stability of resin. The solvent transport properties of the resulting samples were studied in benzene. The combination of natural rubber and the resin exudated from Ailanthus Malabaricum tree can be used to prepare the elastomeric material with suitable properties for specific applications.

Keywords

Natural rubber, Elastomer, Ailanthus Malabaricum tree, Thermogravimetry.

1. INTRODUCTION

Natural rubber is an elastomeric material with excellent elastic properties. The main drawback of the material is its poor stability at high temperature. Chemical modification or blending with suitable additives is the best method to improve the stability of natural rubber. Blending of natural rubber with other thermoplastic polymers has been greatest interest in the field of polymer science to develop the material with better mechanical and thermal stability [1]. Thermoplastic elastomeric blends of natural rubber with polystyrene, polyvinyl alcohol, chitosan, polyethylene etc. are reported in the literature [2-5]. The elasticity of rubber reduced by improving the plasticity was observed with the incorporation of thermoplastic materials. Addition of naturally occurring elastomers is an appropriate solution to enhance the elasticity of natural rubber instead of adding oil. The resin exudated from Ailanthus Malabaricum tree has excellent elastic properties. It is an aromatic amorphous material and can be easily cross-linked by the addition of Dicumyl peroxide [6]. Reports are available on the same resin blended with polystyrene [6]. The elasticity of polystyrene was improved along with reducing the brittleness by the addition of resin. In the present work, resin of Ailanthus Malabaricum tree has been successfully blended with natural rubber with various compositions. Dicumyl peroxide was used as a common crosslinking agent for both the constituent elastomers. The resulting material was introduced for Thermogravimetric and solvent transport studies. As both the elastomers are available in nature, the resulting blend system can be termed as green polymeric material. Tensile studies reveal that the resulting material exhibits excellent elastic properties [7].

2. MATERIALS AND METHODS

2.1 Materials

Natural rubber in the form of sheet was purchased from the rubber plantation located at South Karnataka, India. The Exudated resin was collected from the Ailanthus Malabaricum trees cultivated at the belt of Western Ghats, India. Dicumyl Peroxide and Benzene were supplied by HiMedia Laboratories Pvt. Ltd. Mumbai, India.

2.2 Preparation Methods

Exudated resin was initially dissolved in benzene at room temperature and filtered the solution to remove the non-polymer contents. The solution was then kept for 5 hours to settle down the polymer part at the bottom of the beaker at room temperature. Then the top portion was removed from the beaker and bottom part kept in oven at 60 $^{\circ}$C for 24 hours to evaporate the benzene. The dried sample was used to make the blends. Natural rubber and the elastomeric resin were dissolved in benzene and mixed with suitable blend proportions by using a mechanical stirrer. 2 % (w/w) Dicumyl peroxide (DCP), the cross-linking agent was then accurately weighed and dissolved in benzene. The solution of

Dicumyl peroxide was then slowly added to the blend solution and stirred well for 1 hour. Then the same solution was transferred to the Petri dish and kept in oven at 70 °C for 24 hours. These dried blend samples were peeled out and compression molded using hydraulic press at 10 ton maintained at 140 °C for 20 minutes. The film thickness was reduced to 2 to 2.5 mm. The pure blend samples of various compositions are prepared initially for the comparison with the IPN samples of various blend compositions (weight to weight ratio).

2.3 Thermogravimetric Analysis (TGA)

A Perkin Elmer, Diamond TG/DTG (sensitivity: 0.2 mg) was used to perform the thermo gravimetric analysis of the blended samples. Samples of small amount (1-10 mg) were taken for the analysis and the samples were heated from 40 to 600 °C at a rate of 10 °C/min in nitrogen atmosphere. The TGA and DTG curves were plotted for each sample.

2.4 Swelling Studies

Specimens of the blended samples were weighed properly using an electronic balance. The weighed blend samples were kept in sample bottles with caps to avoid solvent evaporation. Around 20 ml of benzene was taken separately in each of the sample bottles. The bottles were kept in a water bath to maintain a constant temperature. At the end of each interval of the specified time, the blend samples were taken out from the sample bottles to note down the weight. Before weighing the samples wiped out using a tissue paper to remove adhering solvent. The weight was noted until it reaches an equilibrium stage. The experiment was repeated at 55 and 65 °C to study the effect of temperature on solvent uptake. To eliminate the error in the experiment the weighing was completed within 30 seconds.

2.5 X-Ray Diffraction Studies

X-Ray diffraction technique was used to determine the crystalline structure of the prepared polymer blends. X-Ray diffraction patterns of the samples were taken by using a Bruker D8 Advance X-ray diffractometer. The angular range was from $10-40^0$ (2θ). The operating current and voltage of the tube were kept at 20 mA and 40 kV respectively throughout the entire course of investigation.

2.6 Morphology

The surface morphology of the prepared polymer blend samples was analyzed by Scanning Electron Microscopy (SEM) with JEOL JSM 5800LV instrument. In this method, an electron beam directed onto the surface and the emission of electrons from the specimen is detected and amplified to obtain an image. The accelerating voltage is in the range of 1-40 kV and current is 20 micro amperes. The resultant image is often viewed on a video monitor. The resolution achievable ranges down to 2 nm. SEM shows a relatively large depth of field, thus can show topical features better than other microscopic techniques (except perhaps atomic force microscopy). A thin layer (~10nm) of a conductive metal (gold or platinum) is sputtered onto the surface to make the surface conductive.

3 RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

Thermogravimetry is a significant tool used to evaluate the thermal stability of any material. Thermogravimetric curves provide the information about the degradation behavior of any material with increasing temperature. **Figure 1** shows the thermograms of the blends prepared from natural rubber and

exudated resin for various compositions. Exudated resin exhibits thermally least stable material compared to natural rubber. The addition of rubber improves the thermal stability of exudated resin. A considerable enhancement in the thermal stability of resin can be seen in the Thermogravimetric curves by the addition of natural rubber. The thermal stability of the polymeric blend depends strongly on the constituent polymers and blending condition. Formation of interpenetrating polymer networks by creating an entangled structure between rubber and resin molecules during crosslinking of the two phases enhances the thermal stability of the resin. Compared to the nature of degradation of pure components, the blend exhibits a different character. To process a polymer blend, the thermal degradation properties of the individual constituent polymers should be known.
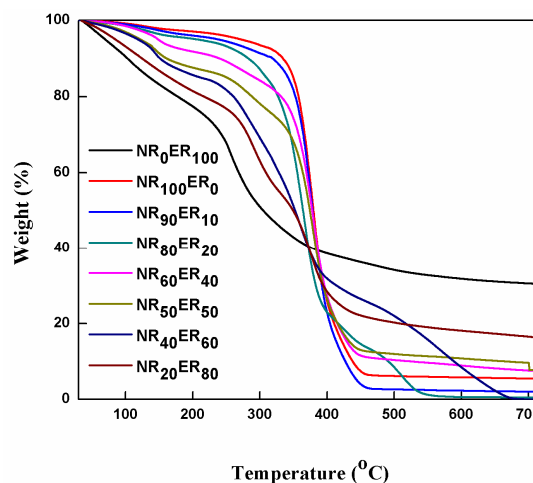
Figure 1. Thermogravimetric curves of NR/ER blends with various compositions

Uncured rubber is highly elastic and thermally very unstable. By the addition of crosslinking agent to natural rubber improves the thermal and mechanical properties. Crosslinked rubber is stable up to 350 °C and further degradation occurs. The weight loss occurs in rubber in two steps. The first step starts from 100 °C to 350 °C is due to the evaporation of bound water molecules in rubber. The degradation or thermal decomposition of rubber initiates at 350 °C and ends at 450 °C. During this stage of degradation it generates 39 % isoprene, 13.2 % dipentene and small amounts of *p*-menthene [8].

Exudated resin exhibits the degradation in a different manner. There are three regions of temperatures in the TGA curve (up to 230, 230-460 and above 460 °C). Weight loss starts from 50 °C and continuous up to the high temperature. It can be seen that, resin has poor thermal stability compared to natural rubber. The weight loss at low temperature is due to the evaporation of solvent and volatile contents. The second stage of weight loss may be due to the degradation of resin by oxidation and chain scission. The residue weight of the resin at high temperature is also comparatively more than that of rubber. The formation of high molecular weight residue particle during decomposition may be the reason for the higher residue weight.

Combination of two elastomers shows a change in the thermal stability of both the individual components. By blending with suitable proportion, it is possible to achieve material with desired properties that lies in between those of two polymers. It is the main advantage of polymer blends. Addition of natural rubber

enhances the thermal stability of exudated resin and the formation of interpenetrating polymer network structure during crosslinking leads to improve the stability by generating an entangled structure between the polymer chains of both the elastomers.

Temperatures at various percentages of weight loss for natural rubber, exudated resin and its blend with different compositions are depicted in **Table 1**. An improvement of 21 °C can be seen at 5 % weight loss by the addition of 20 % NR into ER. Similarly, as we increase the amount of rubber into resin, the temperature value at different weight losses are also increased. The temperatures at weight losses increase with the addition of rubber in to resin. From the enhancement observed in temperature it can be concluded that the incorporation of resin increases the thermal stability of exudated resin. The higher level of interaction between both the elastomeric phases increases the thermal stability of the blends compared to pure exudated resin.

Table 1. Temperature at different weight losses, activation energy of degradation and entropy of various ER/NR blends

Sample	Temperature at different weight losses								Activation energy of degradation E_a, kJ/mol	Entropy ΔS, J/deg/mol
	T_5	T_{10}	T_{15}	T_{20}	T_{25}	T_{30}	T_{35}	T_{40}		
NR	272	334	349	357	362	366	370	373	138	-58
NR90ER10	238	319	341	352	359	364	368	371	135	-67
NR80ER20	205	282	309	326	337	345	350	355	126	-74
NR60ER40	148	239	292	319	332	342	346	351	112	-80
NR50ER50	122	161	250	287	298	326	336	343	90	-84
NR40ER60	118	151	210	260	279	296	313	328	84	-95
NR20ER80	85	124	165	250	262	281	294	308	71	-106
ER	64	97	135	171	217	241	256	268	52	-117

Thermal stability of polymers can be evaluated in terms of activation energy of degradation from TGA curves. The activation energy of degradation was calculated by using the following Horowitz-Metzger equation [9],

$$\ln[-\ln(1-\alpha)] = -\frac{E_a \theta}{RT_s^2} + C \quad \text{(For n = 1)} \qquad (1)$$

where α represents the fraction of weight loss during degradation in time t, $\theta = (T-T_s)$ where T_s is the temperature corresponding to the peak appeared in the DTG curve, E_a is the activation energy of degradation to be calculated and R is the gas constant. The plot of the left-hand side of the Equation 1 versus θ gives a straight line. By the least square method, the kinetic parameters of thermal degradation can be calculated from the slope and the intercept of the straight line.

From the following equation, the pre-exponential factor *A* can be calculated

$$\frac{E}{RT_s^2} = \frac{A}{q \exp\left(\frac{E_a}{RT_s}\right)} \qquad (2)$$

where q is the linear heating rate.

The following relation is used to calculate the entropy of activation

$$A = \frac{kT_s}{h} \exp(\Delta S / R) \qquad (3)$$

where h is Planck's constant and k is Boltzmann constant.

The energy required to decompose the substance is called activation energy of degradation. Higher values in the activation energy indicate more energy should be supplied to decompose the material and hence the material is thermally more stable. The activation energy of degradation increased with increase in rubber content to the elastomeric exudated resin. This indicates the blending of natural rubber with exudated resin improves the thermal stability of resin.

3.2 Water Absorption

It is appropriate to check the ability to resist water molecules of the blend for outdoor application. Natural rubber is hydrophobic and resin shows hydrophilic nature. It is expected to reduce the hydrophilic nature of resin by the addition of hydrophobic rubber. **Figure 2** shows the equilibrium water absorption behavior for different blend ratios. 100 % resin exhibits the higher uptake of water and pure rubber shows the least. In the blend samples, the water is absorbed mainly by resin because rubber is hydrophobic and its water absorbability can be neglected. Pure resin absorbs water immediately but as the percentage of NR increases, time to reach the equilibrium increases. The water absorption can also be minimized by crosslinking the polymer phases. Crosslinked structure reduces the mobility of water molecules by increasing the resistance.
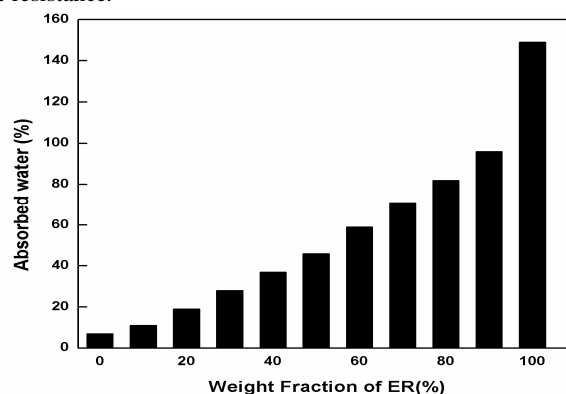

Figure 2. Effect of water absorption on the percentage of ER in NR/ER blends

3.3 Swelling Studies

The ability to transport solvent molecules through the polymer phase is the important property of any polymeric materials. This characteristic of polymers is applicable in the field of technology as ion exchange chromatography, drug delivery, hazardous waste disposal and protective clothing. Transportation or diffusion of small molecules in the polymer mainly depends on temperature, reinforced filler, degree of unsaturation, crosslink density etc. Uncured rubber and resin are soluble in contact with inert solvents especially benzene and toluene. Therefore, the solvent transport behavior cannot be measured in case of pure polymer components without crosslinking. The amount of solvent diffused (Q_t) through the polymer or its blend can be measured at room

temperature using benzene as the solvent. Q_t was calculated using equation

$$Q_t = \frac{M_2}{MW/M_1} \times 100$$

(4)

where M_2 is the mass of solvent absorbed, MW is the molecular weight of the solvent and M_1 is the initial mass of the sample.

Swelling experiment has been conducted for various rubber/resin compositions in benzene. The plots of molar percentage of solvent uptake (Q_t) at room temperature with the square root of time ($\sqrt{t}$) for different blend compositions are as shown in **Figure 3**. Compared to natural rubber the solvent uptake is more for exudated resin. In the initial stage of sorption curve, it can be seen that diffusion of solvent through the elastomers is a fast process and finally attains equilibrium. Molar percentage of solvent uptake of resin reduces with the incorporation of natural rubber. Cross-linked rubber molecules reduce the transport of solvent molecules through the solid phase. The formation of linkage between the macromolecules restricts the rearrangement of the chains easily under solvent stress. The solvent resistance of exudated resin can be easily enhanced by the addition of natural rubber.
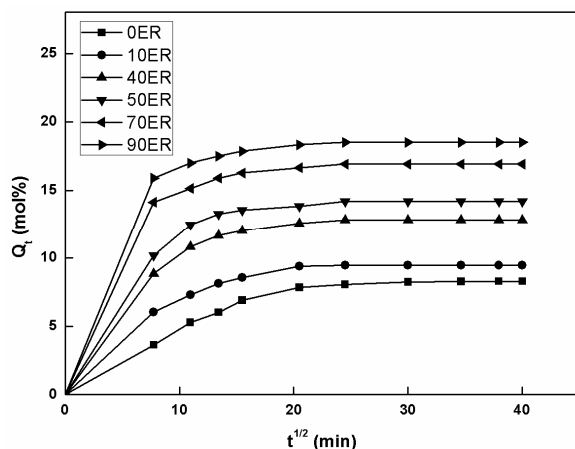
Figure 3. Molar percentage of Solvent uptake with different time intervals for various blend compositions

Evaluation of diffusion coefficient can be done to find the ability to transport solvent molecules through rubbery materials. Diffusion is a kinetic phenomenon related to the size of solvent molecule as a penetrant and to the mobility of polymer segment. The following equation has been used to compute the diffusion coefficient of benzene in rubbery material immersed in an infinite amount of solvent [10].

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2}\right)\sum_{n=0}^{n=\infty}\left[\frac{1}{(2n+1)^2}\exp\left[-D\ (2n+1)^2\pi^2\frac{t}{h^2}\right]\right]$$

(5)

From Equation 5, it is understood that a plot of Q_t versus $t^{1/2}$ is linear for a short time and D can be calculated from initial slope θ. The equation for short time limiting is:

$$\frac{Q_t}{Q_\infty} = \frac{4}{h}\left(\frac{D}{\pi}\right)^{1/2}t^{1/2}$$

(6)

Diffusion coefficient can be calculated by rearranging the above equation

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2$$

(7)

Diffusion is a transport phenomenon in which the rate of change of position or the penetrating ability of solvent molecules through the polymeric material with time can be measured. The plot of diffusion coefficient calculated from the above equation as function of blend composition is as shown in **Figure 4**.

Natural rubber shows more resistant to the transport of solvent molecules and resin exhibited higher solvent diffusivity. Relaxation of polymer chain molecules is required to penetrate or diffuse the solvent through the polymer segment. Polymer chains of resin have the ability to relax more under solvent stress compared to natural rubber. The rigidity of polymer chains decreases by the addition of resin in to natural rubber. It enhances the freedom of polymer chains to the movement of penetrant and hence flexibility reduces. **Figure 4** shows an increase in diffusion coefficient of natural rubber upon the addition of resin.
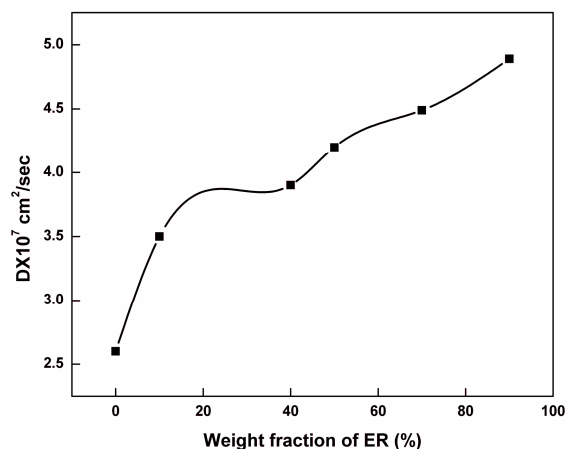

Figure 4. Variation of diffusion coefficient with weight fraction of resin in rubber

3.4 X-Ray Diffraction Studies

To analyze the structural changes of a polymer blend, X-ray diffraction is employed as an advanced technique. Polymers are generally amorphous in nature because of its random orientation of polymer chains. It shows some crystallinity that arises from the regular arrangements of chains even though it has amorphous nature. The coiled structure of elastomer chains is responsible for the highly amorphous nature in case of elastomeric materials. The XRD patterns of natural rubber and its blend with exudated resin is as shown in **Figure 5**.
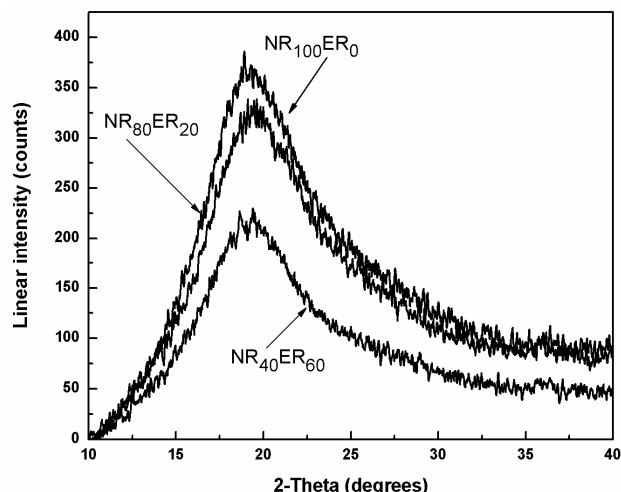
Figure 5. XRD patterns of Natural rubber and its blend with ER.

The crystallinity can be measured by integrating the area under the curve. Natural rubber exhibits slightly crystalline nature and the crystalline peak appeared at 20°. The intensity of the crystalline peak corresponds to rubber reduces by the addition of highly elastic resin phase in the blend. Highly crystalline polymers are more rigid and the material becomes more flexible when the crystallinity reduces.

3.5 Scanning Electron Microscopy

Microphotographs of natural rubber and its blends with resin obtained from scanning electron microscopy are as shown in **Figure 6**. A porous nature or voids can be seen in the morphology of pure rubber. The addition of resin in to natural rubber reduces the porosity by occupying the voids present in rubber. Therefore, a fine morphology is observed for the blends compared to the morphology of natural rubber. The fine morphology enhances the elasticity of rubber by reducing the toughness.

b

c
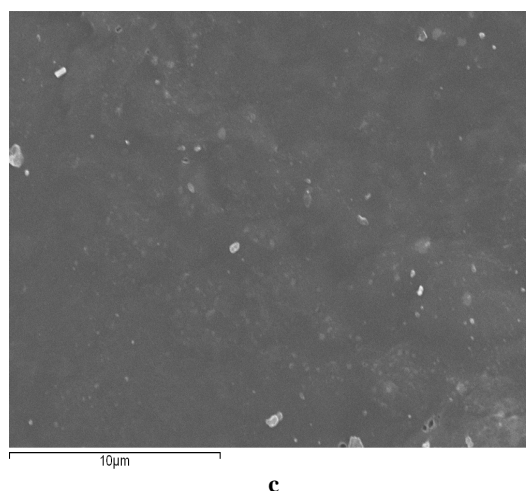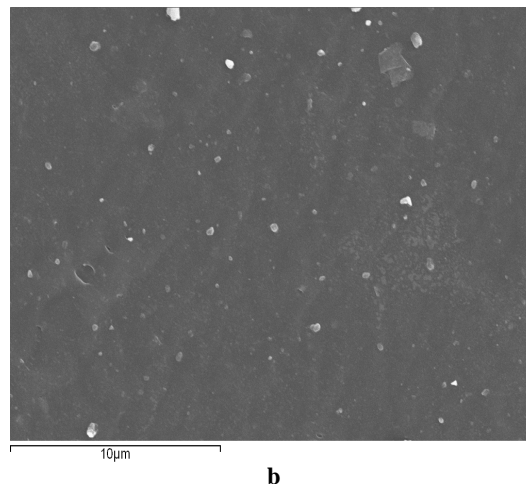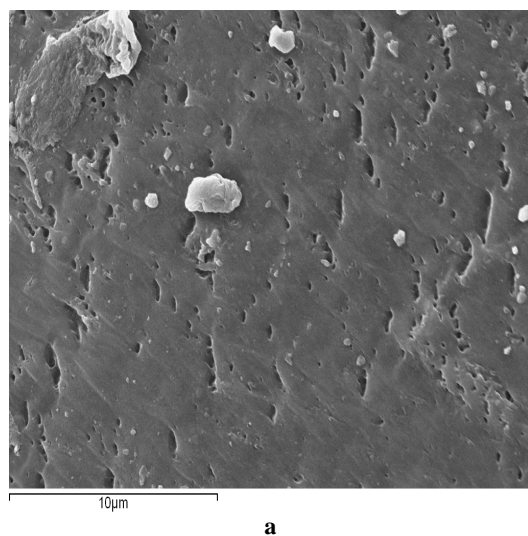
Figure 6. Scanning electron microphotographs of a) natural rubber, b) blend with 40 % of resin and c) blend with 80 % of resin.

4 CONCLUSIONS

Super elastomeric material from natural rubber and exudated resin of Ailanthus Malabaricum tree has been prepared successfully with all possible compositions. The addition of natural rubber enhances the thermal stability of resin. Activation energy of degradation for the resin increased with the incorporation of natural rubber. Solvent transport studies suggest that resin can be used as a softening agent for rubber to improve the elastomeric nature of natural rubber. The reduction in the crystallinity of rubber by the addition of resin was clearly explained in terms of x-ray diffraction patterns. Scanning electron microscopy images supports the same results by improving the morphology along with the addition of resin into rubber.

a

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