

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The research work described in this thesis can be summarized below.

5.1 The Preparation of PPV and OPV

The precursor polymer to the PPV is prepared following the Waessling routes, using a α, α' xylene chloride. Polymerization is carried out in methanol, with sodium hydroxide as a base catalyst. At the end of polymerization, the reaction is quenched by neutralizing the base reaction mixture with dilute HCl to a pH of 7. The PPV film is obtained by heating precursor film at 200°C for 16 h in vacuum. When the Precursor was heated from 30-250°C under nitrogen gas in the scan rate 10°C/min, it showed endothermic broad peak in the DSC result. It is due to the removal of the diethyl sulfide and HCl which converts the PPV precursor to PPV. Then the DSC result of PPV shows the linear line without the endothermic broad curve. TGA results of the PPV exhibit two transitions at 333°C and 526°C. The first transition, at 333°C, is related to the thermal elimination of ethyl sulfide and the second thermal transition, seen at 526°C, is the result of the degradation reaction of PPV. And the confirmation of PPV formation is observed by FTIR. FTIR spectrum of PPV shows characteristic trans-vinylene C-H out of plane bending peak at 964 cm^{-1} . The p-phenylene C-H in plane bending shows at about 1270 cm^{-1} . The other one is located at 1350 cm^{-1} and corresponds to the C-C phenyl ring stretch.

The preparation of OPV carried out by using 2,5-Dimethoxy terephthalaldehyde and (10-dodecyloxyphenyl) acetonitrile. They were dissolved at 70 °C in a mixture of t-BuOH and THF. t-BuOK and n-Bu₄NOH were added quickly and an orange precipitate started to form immediately. t-BuOH and n-Bu₄NOH are bases. The mixture was neutralized by pouring into acidified methanol. The resulting precipitate was dried at 50°C to yield the OPV dyes. The ¹H NMR technique can be used to prove the structure of synthesized OPV. The signals of OPV show at 7.42 (ArH+CH=CCN), 7.2 (ArH), 6.9 (ArH), 3.95 (O-CH₃), 3.87 (O-CH₂), 1.7 (CH), and

1.57-1.33 ppm (=CH₂). The thermal properties of OPV were studied using the differentially scanning calorimeter (DSC). A glass transition of OPV did not show. The melting transition temperature at the maximum heat flow was determined to be about 198.5°C. Thermal gravitation analysis reveals that OPV is thermally degraded with 3 steps at about 135, 266, and 434°C. The first one may be due to the solvent removal, the second transition is to get rid of aliphatic chain, and the last transition reveals the degradation of OPV.

5.2 The Preparation of Grafted Natural Rubber

The grafting of either PPV or OPV onto natural rubber was prepared by free radical polymerization. The rubber macro radical reacted with dye molecules.

The results of NMR led to the calculation for the mole ratio of dye grafted natural rubber using signal areas of NMR spectrum of PPV: isoprene and OPV: isoprene which are 0.99:99.01 and 2.97:97.03, respectively.

In this study, DSC and TG-DTA were used to obtain the thermal properties such as the glass transition temperature, melting temperature, degradation temperature, and weight loss with increasing temperature. The TGA data show that the degradation temperatures of graft copolymers are slightly shifted lower than that of the natural rubber. It means that thermal stability of the graft copolymers was not strongly changed by the small amount of PPV and OPV.

5.3 The Effect of Concentration to Photoluminescence of Copolymers

The PL emission behaviour of natural rubber grafted with various concentrations of either PPV or OPV between 0.5% to 4 wt% (Figure 5.1) shows that if the concentration of PL dye is increased, the red shift increases. It is due to the excimer formation. We can conclude that the higher dye concentrations lead to the aggregation of dye molecules. Figure 5.1 suggests that without PPV and OPV, NR has no clear photoluminescence and the conjugated length increase with either PPV or OPV content.

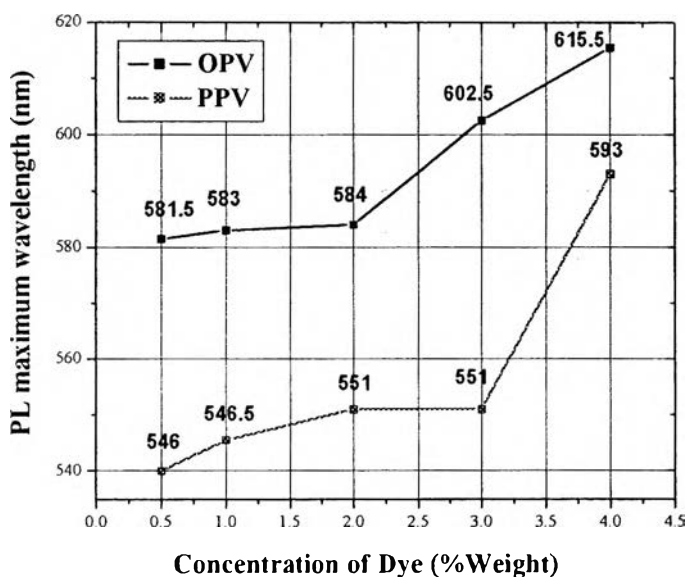


Figure 5.1 PL emission spectra of natural rubber grafted with PPV and OPV at various concentrations. (Excitation at $\lambda=480$ nm for PPV and at $\lambda=520$ nm for OPV).

5.4 The Effect of Percentage Strain to Photoluminescence of Copolymers

The important part of this work is to study the absorption and photoluminescence properties of copolymer as a function of various percentage strains.

For PPV copolymer (Figure 5.2), the red shift is occurred at draw ratio lower than 100%. The explanation for the origin of the strain induced red shift of PPV photoluminescence is that increasing strain increases the conformation order of the polymer chains. This could lead to an increase in the dye molecules close to each other more than increase separation. We can see this effect for natural rubber filled with PPV lower than 3 wt% of PPV. Nevertheless, the copolymer with PPV 3% and 4% by weight, do not show the red shift along with various stresses as see in Figure 5.2. That means the aggregations of dye molecules are broken, even though the stress leads the chains to a high degree of linearization.

The difference between PPV and OPV is the chain length. PPV is macro molecule, but OPV is oligo molecule. Therefore, the solubility of PPV is lower than

OPV. The grafting efficient of OPV is better than PPV as seen in NMR results. More over, the separation ability of OPV is better than the other. It leads to change the emission color.

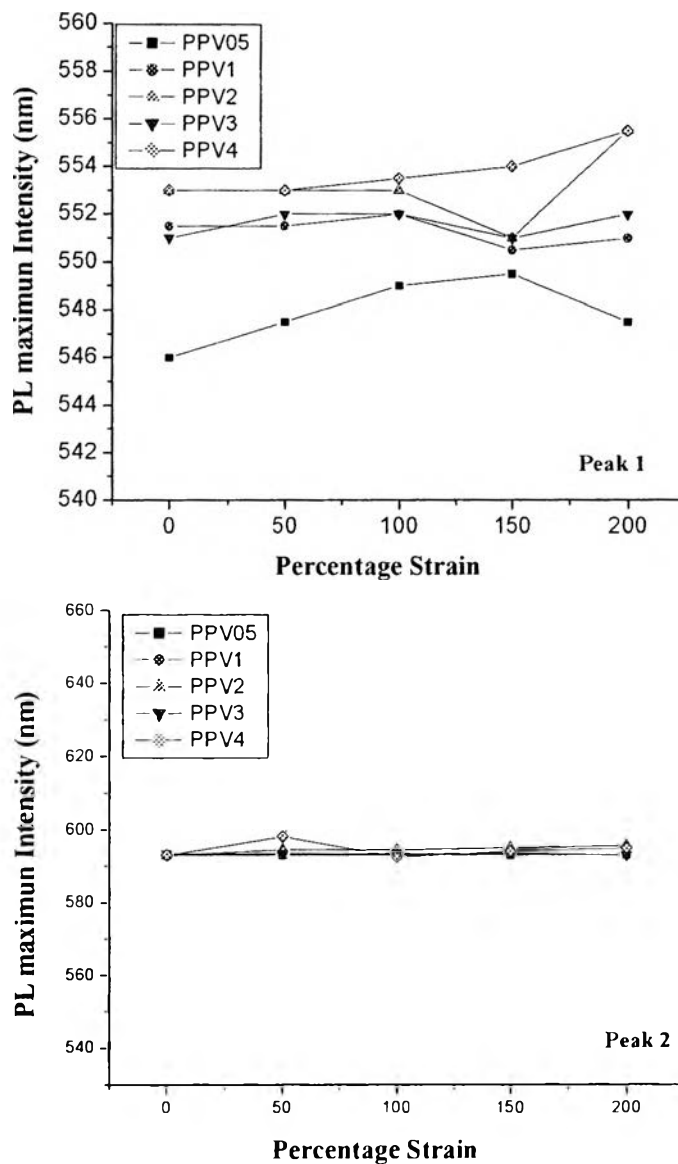


Figure 5.2 PL emission characteristics of natural rubber grafted with PPV 0.5%, 1 %, 2%, 3%, and 4 wt% as a function of various percentage strains (Excitation at $\lambda=480$ nm).

The photoluminescence of NR-OPV copolymers (Figure 5.3) were collected under excitation 520 nm. During initial deformation, natural rubber filled with OPV

0.5%, 1 %, and 2 wt% show red shift behaviour like copolymer of natural rubber and PPV. These results were due to the increased conformation order then the stress allows dye aggregation. The percentage strains 50-200% are not enough to separate the dye molecules but leads to align them to be excimer.

The influences of solid-state tensile deformation on the emission characteristics of natural rubber filled with OPV 3 % and 4 wt% are different from the others, having low concentration of dye. The PL emissions were shifted to shorter wavelength with increasing percentage strain. Their emission changes due to the disruption of the excimers and the emission changes from excimers to isolated excited molecules. This means the conjugation length is shortened.

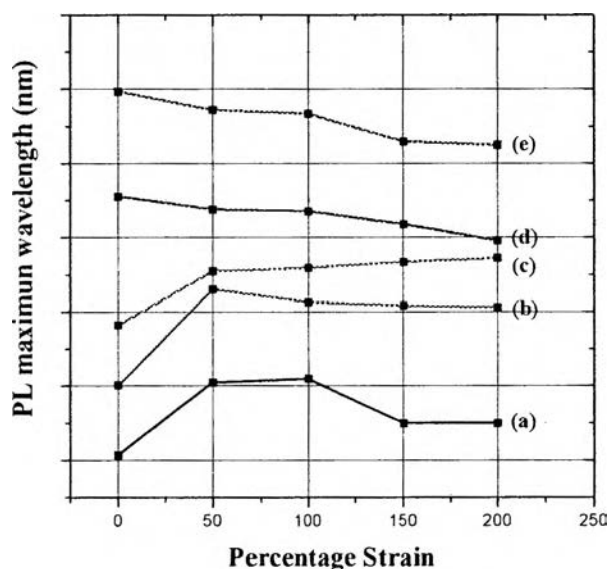


Figure 5.3 PL emission characteristics of natural rubber grafted with OPV (a) 0.5%, (b) 1 %, (c) 2 %, (d) 3 %, and (e) 4 % weight as a function of various percentage strains (Excitation at $\lambda = 520$ nm).

The PL red shift and blue shift can be explained by conjugation model. The conjugation model is based on the free electron theory of conjugated molecules introduced by following equation:

$$E_0 = A + B/L$$

Where E_0 is energy band gap, L is conjugation length of a chain, and A , B are constants. It is seen that PL red shift at the high pressure is due to the elongation of the conjugation length. This may be the same reason why red shift occurred when we apply strain to the copolymers. It is clearly seen that the light emission spectrum could be tuned by not only controlling the dye content but also the percentage strain loaded on samples. Yellow emission is obtained from the molecularly dispersed form, while red emission comes from the aggregated form. Mechanical deformation induces a color change from red to orange-yellow.

5.5 Recommendations

1. The presence of non-rubber contaminants such as protein, etc., could effect the graft copolymerization. Those contaminants, which may act as inhibitor can stop the roles of free radical, Therefore, the elimination of non-rubber contaminated such as protein from natural rubber before graft copolymerization should be done.

2. The synthesis of PPV gives us vary bad smell. To solve this problem, this step should be done in hood or use other routes.