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Adhesive properties of water-soluble and biodegradable hot-melt adhesive based on partially saponified poly(vinyl acetate)

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Abstract
Partially saponified low molecular weight (LMW) PVAc was synthesized and blended with a tackifier for use as hot-melt adhesive with water-solubility and biodegradability. The water-solubility of the partially saponified LMW PVAc was determined as a function of the degree of saponification. PVAc prepared in this study had good water-solubility because its molecular weight was very small and it had lots of hydroxy groups in the polymer chain. As the degree of saponification increased, the solubility of PVAc in water increased. The glass transition temperature and viscoelastic properties of partially saponified PVAc were measured and analyzed by using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). As the temperature increased and the degree of saponification decreased, melt viscosity decreased. The single lap-shear strength and biodegradability of the hot-melt adhesive on based PVAc were systematically evaluated. As the degree of saponification of the polymer increased, the single lap-shear strength of the hot-melt adhesive and the tendency for cohesive failure to occur decreased. The higher the degree of saponification, the faster the rate of biodegradation of the adhesive in natural water.

1. Introduction

Hot-melt adhesives, which have various advantages such as solvent-free and non-toxic characteristics, are convenient for use and satisfy environmental requirements. Therefore, they have been widely used in many applications [1–3]. Hot-melt adhesives are in solid state at room temperature, but liquefied when heated to the application temperature. After these hot-melt adhesives in liquid state are applied, cool rapidly and as a result, the adherends are firmly bound [4, 5]. Thermoplastics, such as poly(ethylene-co-vinyl acetate) (EVA), polyamides, polyolefins, and polyesters, have been used in the formulation of hot-melt adhesives [6–8].

In recent years, the demand for recycling and biodegradation of waste has been increasing. Therefore, in various fields including the bookbinding, there is a high demand for a hot-melt adhesive that can be dissolved in water or biodegradable after the product is discarded [9, 10]. With a wide range of melt index values, good adhesion to a variety of materials, and low cost, EVA has been widely used for hot-melt adhesives, but it is neither water-soluble nor biodegradable. In consideration of environmental issues, several studies have been conducted to use a biodegradable synthetic polymer or a blend of synthetic material and natural polymer as a substitute for EVA. Karan et al. synthesized polyesteramide based hot-melt adhesive from renewable mass such as dimer acid (DA) and catechol, and then investigated the properties of the hot-melt adhesive [11]. Laura et al. developed hot-melt adhesive based on soybean protein isolate and polycaprolactone, which had the improved adhesive strength and biodegradability [12].

Poly(vinyl acetate) (PVAc) is an economically important product with many desirable features, so it has been widely used as an adhesive for wood and paper [13]. Recently, various studies have been conducted to improve the performance of the PVAc adhesive [14–16]. However, these studies have mainly focused on adhesives in the form of waterborne PVAc dispersions. In hot-melt adhesives PVAc cannot be used in the form of a homopolymer and is only used in the form of copolymer (EVA) because it has a low softening point [6, 17].

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Moreover, one major defect in the PVAc adhesives for paper is that it is difficult to remove the adhesive in waste paper. This adhesive can easily adhere to paper-making equipment in the recycling of used papers, so that seriously affect the machine operation and paper quality [18]. The fact that the PVAc adhesive cannot be biodegradable in waste wood is also one of its other disadvantages. The way to improve the water-solubility or biodegradability of polymer is to lower the molecular weight or introduce hydrophilic groups into the polymer chain. Therefore, by adjusting the molecular weight in the polymerization of vinyl acetate (VAc) to lower it and then partially saponifying the polymer to introduce hydroxy groups into the polymer chain, it will be possible to increase the softening point of the polymer and at the same time make the polymer water-soluble and biodegradable. The hot-melt adhesive prepared by using this polymer as a based one will have excellent adhesion to paper and wood products, as well as water-solubility and biodegradability.

In this article, the water-soluble and biodegradable hot-melt adhesive based on partially saponified low molecular weight (LMW) PVAc was studied. We prepared LMW PVAc by solution polymerization of VAc, and partially saponified the polymer with an alkali-ethanol solution. The glass transition temperature and viscoelastic properties of partially saponified PVAc were measured by using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The rheological properties of the polymer were investigated by monitoring the change in the melt viscosity. Finally, the lap-shear strength and biodegradability of the hot-melt adhesive were investigated. Thus, a desirable result was obtained that this hot-melt adhesive can be used as a paper and wood adhesive having water-solubility and biodegradability.

2. Experimental

2.1. Materials

VAc purchased from Shin-etsu Chemical Co. Ltd (Japan) was washed with NaHSO3 aqueous solution and water, dried over anhydrous CaCl2 and distilled under reduced pressure in a nitrogen atmosphere. The initiator azobisisobutyronitrile (Wako Co., Japan) was recrystallized twice in methanol before use. Other extra-pure grade reagents for the solution polymerization of VAc and the saponification of PVAc were purchased from Zhongkejinlong Chemical Limited Company (China). The water used for all procedures was deionized.

H-terpene (DERTOPHENE 1510, Yasuhara Chemical, Inc., Japan) was used as a tackifier. To reduce thermal degradation of the hot-melt adhesive, 0.1 parts by weight of a phenolic antioxidant, Irganox 1010 (Wako Co., Japan), was used as a thermal stabilizer.

2.2. Solution polymerization of VAc

VAc and anhydrous ethanol (0.4v/v) were poured into a three-necked round bottom flask equipped with a stirrer, a dropping funnel and a thermometer, and replaced with nitrogen for 3 h to remove oxygen. The temperature of the reactor was raised to 65 °C, and the reaction solution was gently stirred, while an initiator dissolved in anhydrous ethanol (initiator concentration, 0.03 mol/mol VAc) was slowly added. After the addition of the initiator solution was completed, the reaction mixture was vigorously stirred, while the reaction temperature was not allowed to exceed 70 °C. The samples were taken every 5 min from the reaction mixture to measure its iodine value. The time at which the iodine value no longer changes was set as the end point of the polymerization reaction. After completion of the polymerization, the reaction mixture was poured into a large amount of cold water to separate the resulting polymer from the solvent. The LMW PVAc was washed with water several times and dried under vacuum until a certain weight was reached to remove the solvent and residual monomer contained in the polymer. The conversion was calculated by measuring the weight of the polymer. The conversion was taken the average of five measurement results.

2.3. Partial saponification

LMW PVAc was dissolved in anhydrous ethanol (PVAc:ethanol, 0.05 g g\(^{-1}\)) in a four-necked flask equipped with a reflux condenser, a thermometer, a dropping funnel and a stirrer. The PVAc:ethanol solution in the flask and the 5% sodium hydroxide /ethanol/water (90/10, v/v) solution in the dropping funnel were flushed with nitrogen. The ratio of saponifier/polymer solution was 0.01 (v/v). The alkaline solution was added to the polymer solution under vigorous stirring at 30 °C. After a certain time, the cold water was added to precipitate the polymer, the product was filtered off, and washed with cold water several times. The polymer was dried under vacuum until a constant weight was reached. A quantitative yield of the polymer was obtained.

2.4. Characterization

The molecular weight of the partially saponified PVAc was calculated from the molecular weight of PVAc produced by the acetylation of the polymer. The molecular weight of PVAc was calculated using equation (1) [19]:

\[ M_w = \left( \frac{180}{M_{\text{ac}} + 42} \right) \times M_{\text{ac}} \]
[\eta] = 8.91 \times 10^{-3}[P_n]^{0.62} \text{(in benzene at 30 } ^\circ\text{C)} \quad (1)

where [\eta] is the intrinsic viscosity and \( P_n \) is the number average degree of polymerization of PVAc.

The degree of saponification (DS) of the polymer was determined by the ratio of tertiary butyl and methylene proton peaks in the \(^1\)H NMR spectrum.

The degree of solubility of the polymer in hot water from 50 to 100 \(^\circ\text{C}\) under reflux condition after 3 h was calculated using equation (2) \cite{20}:

\[
\text{degree of solubility} = 1 - \frac{W_f}{W_i}
\]

where \( W_f \) and \( W_i \) are the weight of dried specimens after treatment and before treatment, respectively.

Differential scanning calorimetry (DSC) experiments were performed by a TA Instruments Q-100 differential scanning calorimeter (TA Instruments, Newcastle, USA). All samples are heated from –50 \(^\circ\text{C}\) to 50 \(^\circ\text{C}\) under nitrogen atmosphere. Both the heating rate and cooling rate are 5 \(^\circ\text{C}\) min \(^{-1}\). We used the experimental results in the second run for this paper.

To investigate the viscoelastic properties of partially saponified PVAc, a dynamic mechanical analyzer (Triton 2000 DMA from Triton Technology, Loughborough, UK) was used. The test was performed in the range of –100 \(^\circ\text{C}\) to 75 \(^\circ\text{C}\) under liquid nitrogen. A heating rate is 5 \(^\circ\text{C}\) min \(^{-1}\) and a frequency is 10 Hz.

The viscosity of the materials was measured using a Brookfield DV-II + viscometer (Middleboro, Massachusetts, USA) with increasing temperature.

2.5. Preparation of the hot-melt adhesive

The mixture consisting of the polymer and antioxidant was heated to 150 \(^\circ\text{C}\) and then the tackifier was added. A homogeneous material was obtained by agitation for about 4 h. The rate of polymer and tackifier is 50/50 wt %. LMW PVAc-based hot-melt adhesive films were obtained by compression molding.

2.6. Single lap-shear test

To obtain specimens for lap-shear test, the adhesive joint was obtained by pressing the film between two wood adherend at a temperature of 160 \(^\circ\text{C}\) for 10 min under 30.5 psi of pressing. The bondline thickness was maintained at 0.2 mm. The lap-shear test was performed using a universal testing machine (Instron 4465, Instron, Inc., USA), and the load of the sample to failure was confirmed by according to ASTM D 1002-05. The melted blend was applied to the region to be lapped. The crosshead speed was fixed at 100 mm min \(^{-1}\). The shear strength was taken as the average of three measures.

3. Results and discussion

3.1. The synthesis of LMW PVAc having different degrees of saponification

In order to control the molecular weight of PVAc, in this study, solution polymerization of VAc in ethanol was performed. It is well known that a chain transfer agent must be used to obtain LMW PVAc. Moreover, when a polymer is used in the formulation of a hot-melt adhesive, the chain transfer agent remaining in a trace amount in the polymer may be decomposed at the application temperature, resulting in undesirable effects such as the color change of the adhesive or the volatilization of odor. The chain transfer constant of ethanol is relatively high and it does not lead to any color change and odor, so ethanol was used to obtain a LMW PVAc without the need for a special chain transfer agent. The number average degree of polymerization of PVAc synthesized by solution polymerization in ethanol was 190–210. In general, it is difficult to obtain PVAc with the degree of saponification less than 85% because the reaction rate is accelerated rapidly at the beginning of alkaline saponification reaction of PVAc. In this study, it was possible to obtain PVAc with different degrees of saponification (32.6%, 54.1% and 71.2%, respectively) by adjusting reaction time appropriately under low temperature and alkali concentration.

3.2. Water-solubility

Figure 1 shows the water-solubility of LMW PVAc with different degrees of saponification. As the degree of saponification increased, the solubility of PVAc in water increased. Generally, PVAc is not soluble in water, but poly(vinyl alcohol) is well soluble in water. In the case of partial saponified PVAc, however, its water-solubility depends on the molecular weight of the polymer and the content of hydroxy groups in the polymer chain. PVAc with a normal degree of polymerization (number average degree of polymerization, 1200–1600) begins to dissolve in water only when the degree of saponification is greater than 72%. PVAc prepared in this study was very soluble because its molecular weight is very small and it has lots of hydroxy groups in the chain. PVAc with the degree of saponification of 71.2% had a small solubility at 60 \(^\circ\text{C}\) (12%), but at a temperature higher than that, its solubility increased rapidly and it was completely dissolved in water at less than 90 \(^\circ\text{C}\). The solubility for PVAc with the smallest degree of saponification (32.6%) was 67% at 100 \(^\circ\text{C}\).
3.3. Differential scanning calorimetry

The glass transition temperature, a major indicator of the mobility of segments in the amorphous phase of amorphous and semicrystalline polymers, is often determined by differential scanning calorimetry. Figure 2 shows the thermogram of LMW PVAc specimens having different degrees of saponification. The glass transition temperature for PVAc with the highest degree of saponification (71.2%) is $-19^\circ$C. As the degree of saponification decreased, the glass transition temperature increased. Therefore, PVAc with the degree of saponification of 32.6% had the glass transition temperature of $-2^\circ$C. As shown in the figure, the three specimens showed obvious peaks related to melting between 50 and 100 $^\circ$C. PVAc with the degree of saponification of 71.2% had a sharp melting peak at 89 $^\circ$C. The shape of the peaks became dull as the degree of saponification decreased. Specimens with degree of saponification of 54.1% and 32.6% showed melting points

![Figure 1](image1.png)

Figure 1. Degree of water-solubility of LMW PVAc specimens having different degrees of saponification.

![Figure 2](image2.png)

Figure 2. DSC curves of LMW PVAc specimens having different degrees of saponification.

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of 75 °C and 65 °C, respectively. The hydroxy group formed in the polymer chain during the saponification process of PVAc has a large polarity. Therefore, as the number of hydroxy groups increased, the stiffness of the chain increased, and as a result, the melting point increased.

3.4. Dynamic mechanical analysis
Dynamic mechanical analysis can provide the information on the viscoelastic properties of a polymer. DMA measurements were carried out in the temperature range of −100 °C to 100 °C. Figure 3 shows the storage and loss modulus with temperature measured in LMW PVAc with different degrees of saponification. As shown in the figure, the storage modulus and loss modulus of PVAc with the degree of saponification of 71.2% were the highest. When the degrees of saponification are 71.2%, 54.1%, and 32.6%, the glass transition temperatures obtained from the peaks of the loss modulus are 4 °C, 22 °C, and 25 °C, respectively. These glass transition temperatures are about 25 °C higher than those obtained from DSC. These are in agreement with the general relationship that the glass transition temperature obtained from DMA is 20 °C–30 °C higher than that obtained from DSC. It is interesting that in the case of PVAc having the degree of saponification of 32.6%, the storage modulus and loss modulus are higher than that of 54.1%. It was found that the modulus decreased as the degree of saponification of the polymer decreased at higher temperatures. In all the samples, the storage modulus dropped sharply at the range of 5 to 25 °C, which is associated with the micro Brownian motion of the polymers accompanied by the glass transition, where they changed from a glassy state to a rubbery state.

3.5. Melt viscosity
In a hot-melt adhesive, the thermal stability of the polymer is very important. The information on the thermal stability of a hot-melt adhesive can be obtained by considering the melt viscosity. The decrease in melt viscosity means that the adhesive may be pyrolyzed at the application temperature. If the melt viscosity is low, the application temperature cannot be increased. Figure 4 shows the melt viscosity in LMW PVAc with different degrees of saponification. Melt viscosity values were taken based on values at 1 200 s. As the temperature increased and the degree of saponification decreased, melt viscosity decreased. This is in good agreement with the fact that during the saponification process the degree of polymerization of PVAc decreases and the rigidity of the chain increases due to the formation of hydroxyl groups.

3.6. Single lap-shear strength
Figure 5 shows the single lap-shear strength of hot-melt adhesive as a function of the degree of saponification. The crosshead speed was 100 mm min⁻¹. It is obvious that the single lap-shear strength decreases as the degree of saponification increases. As the degree of saponification of the polymer increased, the tendency for cohesive failure to occur decreased. In the saponification of PVAc, as the degree of saponification increases, its degree of polymerization becomes smaller than the original polymer. When the degree of polymerization, i.e., the
molecular weight decreases, the main destructional form of the adhesive is cohesive failure. Nevertheless, the failure of the hot-melt adhesive with the greatest degree of saponification proceeded to interfacial failure because the intermolecular cohesion increased due to the interaction between hydroxyl groups resulting from the saponification reaction.

3.7. Biodegradation of hot-melt adhesive
First, the films having a thickness of 1 mm were prepared by using PVAc based hot-melt adhesive, and then these were placed in natural water of 20 °C–25 °C and observed. In all specimens after about 1 month, even with the naked eyes, the decomposition process was clearly observed. The higher the degree of saponification, the faster the biodegradation rate of the adhesive. In particular, the specimen with the degree of saponification of 71.2% was completely biodegraded after 4 months, and that with the degree of saponification of 32.6% was completely biodegraded only after 6 months. Also after 0 day, 1 week, 1 month, and 3 months, the surface morphology of the specimens was analyzed using scanning electron microscopy. After 0 day, 1 week, 1 month, and 3 months the surface morphology in the specimen with the degree of saponification of 54% is presented in figure 6. It is

Figure 4. (a) The melt viscosity measured in LMW PVAc with different degrees of saponification; (b) magnification between 130 °C and 180 °C.
obvious that the microorganisms in the water adhered to the surface of the specimen, causing biodegradation of the adhesive. The degree of decomposition increased with time.

4. Conclusions

The solution polymerization of VAc in ethanol was performed. By adjusting the saponification reaction time under low temperature and alkali concentration, PVAc with different degrees of saponification (32.6%, 54.1% and 71.2%, respectively) was obtained. The solubility for PVAc with the degree of saponification of 71.2% at 60 °C was small (12%), but it was completely dissolved in water at less than 90 °C. PVAc with the smallest degree of saponification (32.6%) had the solubility of 67% at 100 °C. In DSC, the glass transition temperatures of the three specimens were −19 °C, −10 °C and −2 °C, respectively, and showed obvious peaks related to melting between 50 and 100 °C. In DMA, when the degrees of saponification are 71.2%, 54.1%, and 32.6%, the glass transition temperatures obtained from the peaks of the loss modulus are 4°C, 22 °C, and 25 °C, respectively,
which are about 25 °C higher than those obtained from DSC. As the temperature increased and the degree of saponification decreased, melt viscosity decreased. As the degree of saponification increased, the single lap-shear strength of the hot-melt adhesive and the tendency for cohesive failure to occur decreased. The higher the degree of saponification, the faster the biodegradation rate of the adhesive. The specimen with the degree of saponification of 71.2% was completely biodegraded after 4 months, and that with the degree of saponification of 32.6% was completely biodegraded only after 6 months.

Currently, we use the hot-melt adhesive based on PVAc with the degree of saponification of 54.1% for book binding and wood bonding. If a book bound with this hot-melt adhesive is discarded, the adhesive can be effectively removed by treating it in a water bath with a temperature of 90 °C for more than 4 h. In the case of wood waste, the adhesive can be biodegraded after 6 months or more under natural conditions.

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**Conflicts of interest**

The authors of this paper have no conflict of interest.

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