Urethane Acrylates for D2T2 Printing System

Hideo Fujii *, Tadakazu Miyata ** and Fumio Jinno **

* Kyoefisha Chemical Co., Ltd.; ** Oji Paper Co., Ltd.
* 2-5, 5-chome, Saikuyo-cho, Nara 630-8453, Japan
** 1-10-6, Shinonome, Koto-ku, Tokyo 135-8558, Japan

The D2T2 (Dye Diffusion Thermal Transfer) printing system, which is famous in video printers, is used widely because of its gradation sequence and instancy. In this printing system, sublimation dye on the ink ribbon is transferred and spread into the receptive layer resin by heat from the thermal head. Since optical density depends on the glass transition temperature (Tg) of receptive layer resin, for high optical density we have to use low Tg resin for the receptive layer. However, when the resin with low Tg is used as the receptive layer resin, the stick-slip behavior becomes worse because the frictional coefficient is high. So, adjustment of the optical density and stick-slip behavior is important.

We have found that UV/EB curable urethane acrylates that consist of the low molecular weight diols (glycols) are useful material to resolve these opposite properties. And we have studied the relationship between the kind of glycols and the properties of the receptive layer resin.

Keywords: UV/EB curable urethane acrylates, low molecular weight diols (glycols), D2T2 Printing System

1. Introduction

Urethane acrylates are known as one of the UV/EB curable oligomers.

Urethane acrylates have been thought that they are flexible and tough because of the aggregation and the crystallization of the hard segments (based on diisocyanate compounds) due to hydrogen bonds (Fig. 1). [1] The hydrogen bonds aren’t too strong to combine each other completely. So, if the power such as strain is added, the hydrogen bonds are broken and are reformed to aggregate and crystallize other hard segments. Numerous kinds of urethane acrylates can be synthesized by changing the raw materials and the combination ratio of these raw materials. Thus it is easy to change their properties to design them to match the specific purpose. Therefore, urethane acrylate are used widely as diverse UV curable inks, coatings (for plastic, wood, optical fiber, paper etc.), electronics material, display and base resin in adhesives.

Fig. 1. Aggregation, crystallization of hard segments

Received March 27, 2004
Accepted May 20, 2004
In this paper, we report our research results about the urethane acrylates for D2T2 printing system which is famous in video printers. In this printing system, the sublimation dye on the ink ribbon is transferred and spread into the receptive layer resin by heat from the thermal head. The thermoplastic resin such as acrylate resin, polyester, polycarbonate and cellulose acetate is used for the receptive layer resin. Since optical density depends on the Tg of the receptive layer resin, for high optical density we have to use low Tg resin for the receptive layer. However, when low Tg resin is used the receptive layer of the record seat becomes soft, or melts, and adheres to the ink ribbon by the heat from the thermal head. Consequently, there is a possibility that printers may not run through at the predefined speed. This phenomenon is called "Stick." Originally, to solve this phenomenon, cross-linking agents such as organic multifunctional isocyanate compounds are added to the receptive layer resin and the cross-linking is formed by heat. This improves the Tg of the receptive layer resin. However, this process is not an efficient method and decreases productivity. Because great energy is needed in order to form the cross-linking, and a special process is needed to complete the cross-linking.

So, we focused attention to UV/EB curable urethane acrylates instead of the thermoplastic resin for receptive layer resin because of its high productivity.

Then, from the result of researching urethane acrylates to be compatible with dyeing property and stick, we have found that UV/EB curable urethane acrylates prepared using glycols are useful. And we have made clear the relationship between the kind of glycols and the properties of receptive layer resin.

2. Method
2.1. Synthesis of Urethane Acrylates

2.1.1. Reaction method

It is known that a hydroxyl group reacts with an isocyanate group to form an urethane bond (Scheme 1). We synthesized urethane acrylates using this reaction.

\[
\text{Hydroxyl group} + \text{Isocyanate group} \rightarrow \text{Urethane bond}
\]

Scheme 1. Reaction of hydroxyl group and isocyanate group

Dihydroxyl compounds (P), (N), diisocyanate compounds (I) and acrylates containing hydroxyl group (H) were used as the raw material, and synthesis was done in two steps (Scheme 2).

In first-step reaction we synthesized urethane oligomers that had isocyanate groups in both ends by making (P), (N) and (I) react. When the measurement value of the concentration of isocyanate groups by the titration reached to the theoretical value, we judged the end of the first-step reaction.

In second-step reaction, (H) was added to the urethane oligomers having isocyanate groups in both ends. When the IR peak of isocyanate groups at 2280 cm\(^{-1}\) disappeared, we judged the second-step reaction was completed.

Scheme 2. Synthesis of urethane acrylates

2.1.2. Sample name and contents of samples

Urethane acrylates were synthesized with the following raw materials and combination ratio is shown in Table 1.
Table 1. Sample name and contents of the sample

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample name</th>
<th>(P)</th>
<th>(N)</th>
<th>(I)</th>
<th>(H)</th>
<th>Unit number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCLDL530</td>
<td>IPDI</td>
<td>2</td>
<td>HEA</td>
<td>2</td>
<td>HEA</td>
<td>2</td>
</tr>
<tr>
<td>Traditionally</td>
<td>U-501L</td>
<td>1</td>
<td>mole</td>
<td>2</td>
<td>mole</td>
<td>2 moles</td>
</tr>
<tr>
<td></td>
<td>U-502L</td>
<td>2</td>
<td>moles</td>
<td>3</td>
<td>moles</td>
<td>2 moles</td>
</tr>
<tr>
<td></td>
<td>U-503L</td>
<td>3</td>
<td>moles</td>
<td>4</td>
<td>moles</td>
<td>2 moles</td>
</tr>
<tr>
<td></td>
<td>U-504L</td>
<td>4</td>
<td>moles</td>
<td>5</td>
<td>moles</td>
<td>2 moles</td>
</tr>
<tr>
<td>Novel type</td>
<td>PCLDL530</td>
<td>NPG</td>
<td>IPDI</td>
<td>HEA</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>U-501LN</td>
<td>1</td>
<td>mole</td>
<td>1</td>
<td>mole</td>
<td>3 moles</td>
</tr>
<tr>
<td></td>
<td>U-502LN</td>
<td>2</td>
<td>moles</td>
<td>2</td>
<td>moles</td>
<td>5 moles</td>
</tr>
<tr>
<td></td>
<td>U-503LN</td>
<td>3</td>
<td>moles</td>
<td>3</td>
<td>moles</td>
<td>7 moles</td>
</tr>
<tr>
<td></td>
<td>U-504LN</td>
<td>4</td>
<td>moles</td>
<td>4</td>
<td>moles</td>
<td>9 moles</td>
</tr>
</tbody>
</table>

PCLDL530: Poly(caprolactone diol (Mw:530))
NPG: Neopentyl glycol
EG: Ethylene glycol
1,4-BD: 1,4-Buthane diol
IPDI: Isophorone diisocyanate
2-HEA: 2-Hydroxyethyl acrylate

The molecular weights of urethane acrylates are changed by changing unit number. The ratio of dihydroxyl compounds and diisocyanate compounds is between 0 and 1.

\[ \frac{(P) + (N)}{(I)} \leq 1 \]

The closer to 0, the smaller molecular weights of urethane acrylates are. The closer to 1, the larger molecular weights of urethane acrylates are.

2.1.3. Difference between traditional type and novel type

![Scheme 3. Scheme of the structure](image)

2.2. Curing method

Urethane acrylates used in this study were coated on the film and cured with EB in the following conditions:

- Acceleration voltage: 175 kV
- Exposure: 4 Mrad
- Oxygen concentration: less than 500 ppm
- Irradiation equipment: EB irradiation equipment (Electro Curtain CB175 / 15/180L, Energy Sciences Inc.)

2.3. Tension test

The cured urethane acrylate film (thickness: 70-100 μm) was cut off in the prescribed size, and these were used as the test piece. And tension test was performed in the following conditions.

- Size of the test piece: 1 cm x 4 cm
- Testing rate: 50 mm/min
- Temperature: 20 °C
- Equipment: SUN RHEO METER (MODEL CR-200D, SUN SCIENTIFIC CO., LTD.)

2.4. Measuring of Tg

DSC measurement was performed for the cured urethane acrylates in the following conditions. And Tg was evaluated from the obtained DSC curve.

- Assessed sample volume: 4–6 mg
- Atmosphere: N₂
- Warming rate: 20 °C/min
- Range of measured temperature: -50 ~ 250 °C
- Equipment: Differential Scanning Calorimeter (DSC-22C and TA-Station-SSC5100), Seiko Instruments, Inc.

2.5. Measuring of the Optical Density

Step printing of black was performed with the color printer (UP-5500, Sony Corporation) at initial applied voltage 2.86V to the sample receptive paper. The transfer concentration in the step 14 was measured with the Macbeth reflection densitometer (RD-914, Sakata Inx Corporation), and the results of the optical density (O.D.) were evaluated as the transfer concentration of the sublimation dye. Target: higher than 2.30.

2.6. Observation of Stick (stick slip behavior)

Sensory evaluation of the generating situation of peeling sound at the time of print and peeling line on the receptive layer was carried out
in five steps.
・「○」, 「○△」: Excellent in Stick
・「△」: Marks were observed
・「△×」: There was peeling sound at the time of print, and peeling line was observed.
(Can't be withstood to practical use)
・「×」: Peeling sound at the time of print was intense, and peeling line was also observed clearly. (Can't be withstood to practical use)
Target: more than 「○△」

3. Results and Discussion
3.1. Measurement results of optical density.
3.1.1. Relationship between unit number and optical density (Traditional type)

Table 2. Relationship between unit number and dying property (Traditional type)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>Dyeing Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-501L</td>
<td>1</td>
<td>1.13</td>
</tr>
<tr>
<td>UF-502L</td>
<td>2</td>
<td>1.35</td>
</tr>
<tr>
<td>UF-503L</td>
<td>3</td>
<td>1.62</td>
</tr>
<tr>
<td>UF-504L</td>
<td>4</td>
<td>1.83</td>
</tr>
</tbody>
</table>

3.1.2. Relationship between unit number and optical density (Novel type)

Table 3. Relationship between unit number and optical density (Novel type)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>Dyeing Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-501LN</td>
<td>1</td>
<td>2.03</td>
</tr>
<tr>
<td>UF-502LN</td>
<td>2</td>
<td>2.27</td>
</tr>
<tr>
<td>UF-503LN</td>
<td>3</td>
<td>2.30</td>
</tr>
<tr>
<td>UF-504LN</td>
<td>4</td>
<td>2.36</td>
</tr>
</tbody>
</table>

From the result of Table 2 and Table 3, we understood that the larger the unit number of urethane acrylates, the better the optical density. Since the cross-linking density would become low when the unit number was large, we considered that it became easy to diffuse the sublimation.

Moreover, we found out that the novel type showed high optical density even in the small unit number of urethane acrylates. We discussed this phenomenon below.

3.1.3. Relationship between glycols and optical density

Since we found out that the optical density of urethane acrylates of the novel type became high, the relationship between the kind of glycols and optical density were evaluated (Table 4).

Table 4. Relationship between glycols and optical density

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>glycol</th>
<th>Dyeing Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-503LN</td>
<td>3</td>
<td>NPG</td>
<td>2.50</td>
</tr>
<tr>
<td>UF-503LE</td>
<td>3</td>
<td>EG</td>
<td>2.40</td>
</tr>
<tr>
<td>UF-503LB</td>
<td>3</td>
<td>1,4-BD</td>
<td>2.25</td>
</tr>
</tbody>
</table>

The result of Table 4 is plotted in Fig. 2. The carbon number between two hydroxyl groups of glycols was indicated on X-axis. Optical density was indicated on Y-axis.

Fig. 2. Relationship between length of glycols and optical density

The result of Fig. 2 showed that there existed linear relationship between optical density and intra-urethane carbon number of glycols.

With assumption that some sublimation dyes were adsorbed onto the urethane bonds, we thought this phenomenon could be explained. Because the shorter the length of glycols, the shorter the intra-urethane distance, so we could consider the sublimation dyes became easy to be adsorbed by the urethane bonds. The results that, under the same unit number, the optical density of novel type showed higher optical density than that of traditional type can be explained by the same reason.
3.2. Results of stick and Tg

3.2.1. Relationship between unit number and properties (Traditional type)

Table 5. Relationship between unit number and properties (Traditional type)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>Stick</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-501L</td>
<td>1</td>
<td>○</td>
<td>52.8</td>
</tr>
<tr>
<td>UF-502L</td>
<td>2</td>
<td>△</td>
<td>43.3</td>
</tr>
<tr>
<td>UF-503L</td>
<td>3</td>
<td>△×</td>
<td>26.8</td>
</tr>
<tr>
<td>UF-504L</td>
<td>4</td>
<td>×</td>
<td>24.6</td>
</tr>
</tbody>
</table>

3.2.2. Relationship between unit number and properties (Novel type)

Table 6. Relationship between unit number and properties (Novel type)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>Stick</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-501LN</td>
<td>1</td>
<td>○△</td>
<td>56.4</td>
</tr>
<tr>
<td>UF-502LN</td>
<td>2</td>
<td>△</td>
<td>60.3</td>
</tr>
<tr>
<td>UF-503LN</td>
<td>3</td>
<td>△</td>
<td>51.4</td>
</tr>
<tr>
<td>UF-504LN</td>
<td>4</td>
<td>△×</td>
<td>50.5</td>
</tr>
</tbody>
</table>

From the result of Table 5 and Table 6, since Tg was in correlation mostly with the stick, we thought we could deal with Tg as a standard of the stick. Moreover, we understood that the larger unit number of urethane acrylates, the lower Tg. Since the cross-linking density would become low when the unit number was large, we considered that the molecule motility during the cross-linking was improved.

Furthermore, with the same unit number when Tg was compared with the traditional type and the novel type, we could see that Tg of novel type was higher (Table 5, Table 6). By using glycols, we considered that since the amount of urethane bonds in one hard segment increased, the power of aggregation and crystallization of hard segments would become large (Fig. 1, Fig. 3). In other words, if the hydrogen bonds of the hard segments became powerful, even if cross-linking density was small, we thought Tg of the urethane acrylates would be high.

![Traditional type](image1)

![Novel type](image2)

Fig. 3. Scheme of the structure No. 2

3.2.3. Relationship between glycols and properties

Table 7. Relationship between glycols and properties

<table>
<thead>
<tr>
<th>Sample name</th>
<th>unit number</th>
<th>glycol</th>
<th>Stick</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF-503LN</td>
<td>3</td>
<td>NPG</td>
<td>△</td>
<td>51.4</td>
</tr>
<tr>
<td>UF-503LE</td>
<td>3</td>
<td>EG</td>
<td>○△</td>
<td>52.9</td>
</tr>
<tr>
<td>UF-503LB</td>
<td>3</td>
<td>1,4-BD</td>
<td>△</td>
<td>48.1</td>
</tr>
</tbody>
</table>

From the result of Table 7, we understood that the shorter the chain length of glycols, the higher Tg and the better stick. We considered that when the glycol of short chain length were used, intra-urethane distance would become short and the power of the aggregation and the crystalization of hard segments would become powerful.

3.3. Results of tension test

![Stress vs. Strain](image3)

Fig. 4. Results of tension test (UF-503L and UF-503LN)

In order to check the change of the kinetic properties by using glycols, we evaluated UF-503L and UF-503LN by tension test and compared the results (Fig. 4).

The novel type showed steeper line than the traditional type at the beginning of the
S.S. curve. This meant that the novel type needed greater power than the traditional type when the test piece would be pulled. We considered these results showed the power of the aggregation and crystallization of the hard segments of the novel type using glycols was more powerful than the traditional type. Therefore, we thought the Novel type was advantageous to the stick.

4. Conclusions

We could be compatible with dyeing property and Tg by using glycols. There exists linear relationship between dyeing property and intra-urethane carbon number of glycols. These results can be explained by the assumption that dye molecules would be adsorbed on the part of the hard segments improved by glycols.

Acknowledgments

The authors thank emeritus professor M. Tsunooka and professor M. Shirai at Osaka Prefecture University for their valuable suggestions in writing this manuscript.

References