Abstract: For the application of low-temperature curing on automotive clearcoats, isocyanate cross-linkers blocked with imidazole derivatives were newly synthesized. The effect of the alkyl groups in the imidazole derivatives on the deblocking behavior and curing kinetics was investigated. The free isocyanate groups exposed by the deblocking of imidazole-based blocking agents were monitored by real-time Fourier-transform infrared spectroscopy. The bond dissociation energy, activation energy of deblocking, and H–N distance were interpreted through density functional theory simulation of various imidazole-based blocked isocyanates. To evaluate their applicability to automotive clearcoats, the synthesized imidazole-based blocked isocyanates were mixed with a polyol binder containing hydroxyl groups, and the clearcoat samples were cured at relatively low curing temperatures (100, 110, and 120 °C). The real-time storage modulus was measured using a rotational rheometer to elucidate the thermal curing dynamics by the blocking agents. In addition, the surface hardness of the cured clearcoat layers, which is affected by the chemical structure of the imidazole derivatives, was evaluated by nanoindentation test. In-depth analyses of the deblocking behaviors and thermal curing properties of clearcoats using imidazole-based blocked isocyanates demonstrated that the newly developed coating system could be suitably applied for the development of low-temperature curing technology.

Keywords: automotive clearcoat; blocked isocyanates; low-temperature curing; imidazole blocking agent; cross-linking properties; urethane reaction; DFT simulation

1. Introduction

Automotive coatings including electrocoat, primer, basecoat, and clearcoat layers must possess special functions that are responsible for the outer surface of the car [1]. Clearcoat, a hard and transparent layer coated on the outermost surface, is used to protect the inner coating layers and
frames and improve the exterior appearance \[2,3\]. They should be densely cross-linked to adequately defend against external damages such as acid rain, washing brushes, and bird or oil droppings \[4–6\]. The existing thermal curing processes for automotive clearcoats are operated at high temperature conditions (e.g., 30–40 min at 150 \({}^\circ\)C) \[7\]. Considering the high energy consumption and ecological issues associated with the curing process, newly modified clearcoat materials that can be cured at relatively low temperatures, guaranteeing sustainable physical and chemical properties, are being explored in the automotive industry \[8,9\].

Most automotive clearcoat compositions are based on urethane-based coating systems, forming cross-linked networks between a polysisocyanate (NCO) cross-linker and a polyol binder containing hydroxyl (OH) functional groups \[10,11\]. Their superior physical and chemical resistances prove that the existing urethane-based coating technology is quite favorable for fabricating automotive clearcoats. In addition, the antiweathering properties of urethane-based clearcoats provide the relief of long-term management of automotive bodies \[12\]. These systems, widely applied in coating industries, can be generally tuned by varying the chemical structural configuration of a polymeric polyol resin and an isocyanate cross-linker.

NCO groups in the isocyanate-based cross-linker are typically blocked with a specific molecule (i.e., blocking agent) to prevent them from immediately reacting with moisture and nucleophiles \[13,14\]. During the thermal curing process, the blocking agent can be easily detached from the blocked isocyanate cross-linker to trigger the urethane-bonding reaction. The dissociation temperature of the blocking agent is substantially affected by its chemical structure. Previous studies have reported that blocking agents containing strong electron-withdrawing groups expedite the curing reaction by being dissociated at relatively lower temperatures, but those with strong electron-donating groups hinder the reaction because of the higher bond dissociation energy involved \[15,16\]. Reflecting the upcoming novel applications of low-temperature curing of automotive clearcoats, it is necessary to elucidate the relationship between the chemical structures of blocking agents and their cross-linking reactivity.

There are many studies in the literature investigating the effect of blocking agents on the cross-linking features of urethane-based coating systems \[17,18\]. The chemical configurations of blocking agents can dominantly affect their dissociation from blocked isocyanate cross-linkers, eventually differentiating the cross-linking properties of thermally cured coating layers. Typically, pyrazole-, oxime-, phenol-, and malonate-based materials are widely utilized as blocking agents owing to their specific chemical structures that result in unstable bond linkages. Their ring-like structure pulls electrons from the bondage site, which is effective in lowering the deblocking temperature. In addition, it has been shown that the size of the substituent attached to the blocking agent adjusts the electrochemical properties, thereby significantly changing the deblocking temperature.

In-depth investigation of the cross-linking properties of clearcoats by newly adapting blocking agents is necessary to develop an economic and environment-friendly curing process \[19,20\]. Imidazole derivatives can be regarded as promising blocking agents because of their low toxicity \[21\] in building the eco-friendly coating processes with low emission of volatile organic compounds (VOCs). Jung et al. \[22\] recently introduced the usefulness of imidazole derivatives for blocked isocyanate cross-linker that can improve thermal stability and mechanical properties of cross-linked coatings by the additional imidization reaction.

In this study, the deblocking behavior and thermal curing performance of isocyanate cross-linkers blocked with different imidazole derivatives were investigated. Four types of imidazole-based blocking groups (i.e., imidazole (Imi), 2-methylimidazole (MI), 2-ethylimidazole (EI), and 2-isopropylimidazole (IPI)) were prepared and attached to a hexamethylene diisocyanate isocyanate (HDI) trimer having three NCO groups per molecule. The free NCO groups available after the deblocking stage of imidazole-based blocked isocyanates (imidazole-BIs) were monitored with increasing temperature, employing a Rheonaut module and Fourier-transform infrared spectrometer (FT-IR) \[23,24\]. Density functional theory (DFT) simulations for imidazole-BIs were conducted to predict the activation energy required for deblocking and the H–N distance in the imidazole molecule, which are significantly
influenced by the chemical structure of the blocking groups [25,26]. The real-time cross-linking dynamics of clearcoats cured with imidazole-BIs were examined using a rotational rheometer under the small-amplitude oscillatory shear (SAOS) mode [9,27,28]. Furthermore, a nanoindentation tester (NHT) showed distinguishable surface properties of clearcoat films cured with given imidazole-BIs [29–31].

2. Materials and Methods

2.1. Preparation of Clearcoats

2.1.1. Materials

Imidazole (Imi), 2-methylimidazole (MI), 2-ethylimidazole (EI), and 2-isopropylimidazole (IPI) were supplied by Sigma Aldrich (St. Louis, MO, USA). Propylene glycol methyl ether acetate (PMA) and 1-butanol were also obtained from Sigma Aldrich and used without further purification. Commercialized polyester polyol (KOH value = 270 mg KOH/g, nonvolatile portion = 60%) as a polymeric binder was provided by KCC Co. Ltd. (Yongin, Korea). The Desmodur® N3300 hexamethylene diisocyanate (HDI) trimer and Desmodur® PL350 (commercial blocked isocyanate cross-linker) were obtained from Covestro (Leverkusen, Germany).

2.1.2. Synthesis of Isocyanate Cross-Linkers Blocked with Imidazole Derivatives

The chemical structures of imidazole-based blocking agents and synthesized imidazole-BIs are portrayed in Figure 1a. The first step for synthesizing imidazole-BIs was to mix imidazole derivatives and solvent PMA (Imi 0.36 g and PMA 0.91 g; MI 0.44 g and PMA 0.96 g; EI 0.51 g and PMA 1.01 g; and IPI 0.59 g and PMA 1.06 g, respectively) at 60 °C under a nitrogen atmosphere. The mixtures were then stirred for 2 h after adding 1 g HDI trimer. From the disappearance of the isocyanate peak (2250–2280 cm\(^{-1}\)) in the FT-IR (Nicolet 6700/Nicolet Continuum, Thermo Fisher Scientific, Waltham, WA, USA) spectra of the imidazole-BIs, it was confirmed that imidazole derivatives were successfully attached to the isocyanate functional groups in HDI (Figure 1b). All BI cross-linkers were mixed in a volatile solvent (1-butanol) with solid contents of 60% to reduce the viscosity. Additionally, the curing properties of the commercial PL350 cross-linker, which is mainly incorporated at the conventional curing temperature of 150 °C, were compared with those of synthesized imidazole-BIs.

![Figure 1. (a) Schematic of the combination of isocyanate cross-linkers with imidazole derivatives and (b) FT-IR absorbances of imidazole-based blocked isocyanates (imidazole-Bis) and free hexamethylene diisocyanate isocyanate (HDI).](image-url)
2.1.3. Formulation of Clearcoats with Imidazole-BIs

Clearcoat samples were formulated to investigate the reactivity and thermal curing performance of the prepared imidazole-BIs. Each clearcoat was made by adding each BI (2.11 g for BI-Imi, 2.22 g for BI-EI, 2.34 g for BI-MI, and 2.87 g for BI-IPI) to 1 g of a polyol resin. For comparison, another clearcoat sample was prepared by mixing 1.54 g PL350 and 1 g polyol resin. The amounts of each BI and polyol were based on a 1:1 molar ratio between the NCO group in the BI and the OH group in the binder. In addition, 0.016 g of BYK-306 (BYK Chemie, Wesel, Germany) was inserted to the clearcoats as a leveling agent. The formulations of various clearcoat samples with different BIs are listed in Table 1.

Table 1. Formulation of clearcoat samples with different imidazole-based blocked isocyanates (imidazole-Bis).

| Clearcoats          | CC-Imi | CC-MI | CC-EI | CC-IPI | CC-PL350 |
|---------------------|--------|-------|-------|--------|----------|
| Polyester polyol    |        |       |       |        |          |
| (NV = 60%)          | 1 g    |       |       |        |          |
| Blocked isocyanate  |        |       |       |        |          |
| (BI)                |        |       |       |        |          |
| BI-Imi              | 2.11 g | -     | -     | -      | -        |
| BI-MI               | -      | 2.22 g| -     | -      | -        |
| BI-EI               | -      | -     | 2.34 g| -      | -        |
| BI-IPI              | -      | -     | -     | 2.87 g | -        |
| BI-PL350            | -      | -     | -     | -      | 1.54 g   |
| BYK 306             |        | 0.016 |       |        |          |
| Total               | 3.126 g| 3.236 g| 3.356 g| 3.886 g| 2.556 g |

2.2. Characterization Methods

2.2.1. In-Situ FT-IR Analysis

The real-time FT-IR spectra indicating the temporary structural changes of BIs at the molecular level were marked using a Rheonaut FT-IR module (Thermo Scientific Inc., Waltham, WA, USA). The deblocking behavior of the imidazole-based blocking agents was analyzed by measuring the change in isocyanate absorbance band with increasing temperature. Contour maps and 3-D image data that quantify the amount of free isocyanate groups were obtained under a specific sequential thermal condition: isothermal 30 °C for 3 min and ramp rate of 5 °C/min to 150 °C with 2 scans at a resolution of 4 cm⁻¹.

2.2.2. Density Functional Theory (DFT) Simulation

The geometric configurations and the chemical bonding characteristics of the imidazole-BIs were optimized using density functional theory (DFT) simulations implemented in the Gaussian 09 software at the B3LYP/6-31G(d) level. Using optimized structures of BIs, the bond dissociation energy (BDE) and activation energy ($E_a$) for dissociating imidazole blocking agents in the BIs were calculated. BDEs and $E_a$ provide information on the enthalpy difference between the products and reactants and the Gibbs free energy difference between the reactants and transition state, respectively. The transition states were identified by scanning the distance between H–N, revealing that their structure had only one imaginary frequency. The electrostatic potential map and geometric configuration of imidazole-BIs were then illustrated to determine the distribution of electrons and the distance between atoms inside their structures [25,26].

2.2.3. Measurement of Real-Time Rheological Properties of Various Clearcoats

The macroscopic curing dynamics of clearcoats containing imidazole-BIs were monitored using a rotational rheometer (MARS III, HAAKE, Thermo Scientific, Waltham, WA, USA) equipped
with a heating chamber. The real-time storage (or elastic, $G'$) modulus was measured under the small-amplitude oscillatory shear (SAOS) mode to understand transient cross-linking behaviors of clearcoat materials. During several iterative tests per one sample to ensure reliable rheological data, the angular frequency and the strain were fixed as 5 Hz and 0.5% based on the gap (500 µm) between the upper and lower plate, respectively. The thermal condition was controlled in the chamber; increasing the temperature from 30 to 100, 110, and 120 °C, respectively, at 10 °C/min and then consistently maintaining at the corresponding temperatures. More detailed information about the real-time rheological properties of clearcoat systems during the thermal curing process was described in the literature [27,28,30,31].

2.2.4. Measurement of Surface Mechanical Properties of Cured Clearcoat Films

The surface resistance of the clearcoat films cured with imidazole-BIs was determined using a nanoindentation tester (NHT3, Anton Paar, Graz, Austria) [29–31]. Clearcoat films of 100 µm thickness were fabricated through the bar coating method and curing at 100, 110, and 120 °C, respectively, in a convection oven for 20 min. Indentation penetration depths on the surfaces of the cured films were obtained via vertical load operation. The load was applied on the film surface until it reached a maximum value of 10 mN and after a 10 s pause time at that load, it was gradually removed from the surface for the film recovery. The loading and unloading rates of the indenter during the measurement were set to 19.8 mN/min. The surface hardness (HIT) of cured clearcoat films, which represents the applied force over projected area, was calculated based on Oliver and Pharr method [29].

3. Results and Discussion

3.1. FT-IR Analysis for the Dissociation of Imidazole-BIs

The amount of free isocyanate groups available after the deblocking of imidazole derivatives was estimated in real-time using the Rheonaut module equipped with FT-IR spectroscopy. As depicted in Figure 2a, the absorbance attributed to the free NCO group (2250–2280 cm$^{-1}$) in the four imidazole-BIs, increased by rising the temperature at a ramp rate of 5 °C/min, confirming the deblocking transition of imidazole derivatives. BI-IPI exhibited the highest absorbance in comparison to other imidazole-BIs. To quantitatively compare the deblocking behaviors of imidazole derivatives under the assigned temperature conditions, the free NCO group of all imidazole-BIs was normalized on the basis of the C=O peak value (1540~1870 cm$^{-1}$) (Figure 2b). The ratio of NCO/C=O represents the relative amount of free NCO groups exposed by the dissociation of blocking agents from imidazole-BIs. As the temperature gradually increased, the amount of free NCO groups also increased for all imidazole-BIs, in the order of BI-IPI > BI-EI > BI-MI > BI-Imi. However, the NCO/C=O ratio of PL350 was the lowest because it is designed to be activated around a curing temperature of 150 °C.
As the alkyl substituent on the imidazole derivative gets bulky, the distance (solid arrow in Figure 3b) to predict the efficiency of the deblocking reaction. It can be seen that BDE and $E_a$ steadily decreased as the alkyl group in the imidazole derivatives became bulkier. To interpret this result, the C–N charge difference in each imidazole-BI was further calculated, but this was found to be not much influenced by the size of the alkyl group in imidazole derivatives. In the electrostatic map of Figure 3b, the negatively charged O and N atoms are red colored and positively charged H atom is blue colored. As the alkyl substituent on the imidazole derivative gets bulky, the distance (solid arrow in Figure 3b) between O and N atoms obviously increases due to the steric effect that makes the repulsion between them even greater. This phenomenon eventually shortens the H–N distance designated by dashed arrow in Figure 3a, thereby lowering the activation energy for the deblocking reaction.

The dissociation of the blocking agents is closely linked to the structure of the alkyl group located in the 2-position of the imidazole derivatives. The BI-Imi has an H in the 2-position, leading to a very low NCO/C=O value even at high temperatures. As the alkyl group in the 2-position got bulkier (e.g., methyl group (CH$_3$) in BI-MI and ethyl group (C$_2$H$_5$) in BI-EI), the amount of free NCO groups available increased. For BI-IPI, the blocking agent started to separate at a much lower temperature owing to the bulky size of the alkyl group which increases the steric effect, resulting in the largest amount of free NCO groups in the high-temperature regime (NCO/CO > 0.6).

### 3.2. DFT Calculations of Imidazole-BIs

From the DFT simulations, the reactivity of various imidazole-BIs was predicted at the molecular level. The BDE and $E_a$ were calculated (Table 2) using the optimized chemical structures of imidazole-BIs (Figure 3a), to predict the efficiency of the deblocking reaction. It can be seen that BDE and $E_a$ steadily decreased as the alkyl group in the imidazole derivatives became bulkier. To interpret this result, the C–N charge difference in each imidazole-BI was further calculated, but this was found to be not much influenced by the size of the alkyl group in imidazole derivatives. In the electrostatic map of Figure 3b, the negatively charged O and N atoms are red colored and positively charged H atom is blue colored. As the alkyl substituent on the imidazole derivative gets bulky, the distance (solid arrow in Figure 3b) between O and N atoms obviously increases due to the steric effect that makes the repulsion between them even greater. This phenomenon eventually shortens the H–N distance designated by dashed arrow in Figure 3a, thereby lowering the activation energy for the deblocking reaction.

**Table 2.** Calculated BDE, $E_a$, C–N charge difference, and H–N distance for imidazole-Bis.

| Blocked Isocyanate | BDE (kcal/mol) | $E_a$ (kcal/mol) | C–N Charge Difference | H–N Distance (Å) |
|-------------------|----------------|----------------|-----------------------|------------------|
| BI-Imi            | 13.78          | 53.7217        | 1.303                 | 2.486            |
| BI-MI             | 13.08          | 53.1877        | 1.302                 | 2.477            |
| BI-EI             | 12.89          | 52.9882        | 1.303                 | 2.473            |
| BI-IPI            | 12.52          | 52.9066        | 1.301                 | 2.472            |
3.3. Real-Time Curing Behaviors of Clearcoats with Imidazole-BIs

Figure 4 shows the macroscopic curing behaviors of the clearcoats prepared with imidazole-BIs or BI-PL350 and a polyester polyol at three different curing temperatures: 100, 110, and 120 °C. The curing dynamics were observed at temperatures lower than the conventional operating temperature (150 °C), to evaluate the possible applications of low-temperature curing technology. Under the given temperature conditions, CC-Imi and CC-PL350 failed to form a cross-linked polyurethane network, indicating that the applied thermal energy was insufficient to separate the blocking agent from the HDI trimer. In contrast, the curing rate and cross-linking density with CC-IPI were noticeably superior to other BIs, especially at 100 °C (Figure 4a), addressing that the IPI blocking agent was extensively dissociated from the isocyanate group in the BI even at relatively low temperatures. At 110 and 120 °C, the storage modulus values of clearcoats using CC-EI and CC-MI got closer to that of CC-IPI (Figure 4b,c).
3.4. Surface Mechanical Properties of Cured Thin Clearcoat Films

The mechanical properties of the surfaces of clearcoat films cured with imidazole-BIs were investigated to judge the industrial applicability of low-temperature coating systems. Figure 5a–c shows the indentation penetration depth profiles of the clearcoat films cured at 100, 110, and 120 °C, respectively, obtained via the nanoindentation test along the loading-pause-unloading stages of the indenter. Under all temperature conditions, the indentation depth profiles for CC-IPI and CC-EI films were similar, exhibiting that the BIs with relatively large-sized blocking agents had reacted actively. The CC-MI was softer than the other two clearcoat films because of its lower cross-linking density. Note that the indentation data for CC-Imi were not meaningful at all curing temperatures, which was attributed to the inactive deblocking of BI-Imi.

![Figure 5. Cont.](image-url)
The HIT (indentation hardness, Figure 5d) values calculated from the normal force vs. penetration depth curves, based on Oliver and Pharr method [29], are a quantitative estimation of surface mechanical properties. Note that the HIT values for CC-PL350 were obtained at 140 and 150 °C because it could not be cured at lower temperatures. To achieve the HIT level of CC-PL350 at 150 °C, which is considered as the reference value that meets industrial targets, the CC-MI film should be cured above 120 °C. When cured at temperatures above 110 °C, clearcoat films with BI-IPI and BI-EI exerted higher HIT values than that of the base CC-PL350. The surface mechanical properties of these cured films substantiate that clearcoats employing imidazole-BIs can be positively applied in industrial fields because of their competent curing performance even at relatively low curing temperatures.

4. Conclusions

The effects of the structural configuration of imidazole-based blocking agents on the degree of their dissociation from blocked isocyanate cross-linkers and cross-linking behavior of clearcoats during the thermal curing process were investigated using various experimental methods. The chemical structure of the imidazole-based blocking agents, based on the size of the alkyl group, significantly affected the deblocking behavior and curing characteristics. As the alkyl group in the blocking agent became bulkier, the free isocyanate groups in the blocked cross-linkers were found to be more exposed owing to the active dissociation of the blocking agent. DFT simulation results of the imidazole-BIs theoretically demonstrated that large-sized substituents in imidazole derivatives can significantly decrease the activation energy and bond dissociation energy, effectively triggering the urethane cross-linking reaction in clearcoats. The thermal curing dynamics in terms of real-time storage modulus data of the clearcoats indicated that using an imidazole-based blocking agent with a larger substituent resulted in a faster curing reaction. The surface hardness of the clearcoat films cured by imidazole-BIs was highly dependent on the steric effect of the blocking agents; the one with a bigger sized substituent resulted in the formation of a harder cross-linked surface. Imidazole-BIs can, therefore, play an important role in developing low-temperature curing technology for automotive clearcoats because of their active deblocking reaction and suitable thermal curing properties.

Author Contributions: Conceptualization, T.H.L. and S.M.N.; methodology, M.C.; software, M.H.; validation, W.H., H.W.J., and S.M.N.; formal analysis, M.C. and M.G.K.; investigation, T.H.L. and K.I.J.; resources, M.C. and T.H.L.; data curation, M.C. and K.I.J.; writing—original draft preparation, M.C. and K.I.J.; writing—review and editing, K.I.J. and H.W.J.; visualization, M.G.K.; supervision, H.W.J. and S.M.N.; project administration, H.W.J. and S.M.N.; funding acquisition, W.H., H.W.J., and S.M.N. All authors have read and agreed to the published version of the manuscript.
**Funding:** This study was supported by the Ministry of Trade, Industry & Energy (MOTIE, Korea) under Industrial Technology Innovation Programs (No. 10067706 and No. 20010256) and the Korea Research Institute of Chemical Technology (KRICT) Research and Development (R&D) program.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Doerre, M.; Hibbitts, L.; Patrick, G.; Akafuah, N.K. Advances in automotive conversion coatings during pretreatment of the body structure: A review. *Coatings* 2018, 8, 405. [CrossRef]
2. Slinckx, M.; Henry, N.; Krebs, A.; Uytterhoeven, G. High-solids automotive coatings. *Prog. Org. Coat.* 2000, 38, 163–173. [CrossRef]
3. Poth, U. *Automotive Coatings Formulation: Chemistry, Physics und Practices*, 1st ed.; Vincentz Network GmbH & Co KG: Hanover, Germany, 2008.
4. Tahmassebi, N.; Moradian, S.; Mirabedini, S.M. Evaluation of the weathering performance of basecoat/clearcoat automotive paint systems by electrochemical properties measurements. *Prog. Org. Coat.* 2005, 54, 384–389. [CrossRef]
5. Ramezanazdeh, B.; Mohseni, M.; Yari, H.; Sabbaghian, S. A study of thermal–mechanical properties of an automotive coating exposed to natural and simulated bird droppings. *J. Therm. Anal.* 2010, 102, 13–21. [CrossRef]
6. Yari, H.; Moradian, S.; Tahmasebi, N. The effect of basecoat pigmentation on mechanical properties of an automotive basecoat/clearcoat system during weathering. *Polym. Degrad. Stabil.* 2009, 94, 1281–1289. [CrossRef]
7. Akafuah, N.K.; Poozesh, S.; Salaiimeh, A.; Patrick, G.; Lawler, K.; Saito, K. Evolution of the automotive body coating process—A review. *Coatings* 2016, 6, 24. [CrossRef]
8. Mayyas, A.; Qattawi, A.; Omar, M.; Shan, D. Design for sustainability in automotive industry: A comprehensive review. *Renew. Sustain. Energy Rev.* 2012, 16, 1845–1862. [CrossRef]
9. Kim, B.; Lee, D.G.; Kim, D.Y.; Kim, H.J.; Kong, N.S.; Kim, J.C.; Noh, S.M.; Jung, H.W.; Park, Y.I. Thermal radical initiator derivatives based on O-imino-isourea: Synthesis, polymerization, and characterization. *J. Polym. Sci. Pol. Chem.* 2016, 54, 3593–3600. [CrossRef]
10. Groenewolt, M. Polyurethane Coatings: A perfect product class for the design of modern automotive clearcoats. *Polym. Int.* 2019, 68, 843–847. [CrossRef]
11. Chattopadhyay, D.K.; Raju, K. Structural Engineering of polyurethane coatings for high performance applications. *Prog. Polym. Sci.* 2007, 32, 352–418. [CrossRef]
12. Hill, L.W.; Korzeniowski, H.M.; Ojunga-Andrew, M.; Wilson, R.C. Accelerated clearcoat weathering studied by dynamic mechanical analysis. *Prog. Org. Coat.* 1994, 24, 147–173. [CrossRef]
13. Wicks, D.A.; Wicks, Z.W., Jr. Blocked isocyanates III: Part B: Uses and applications of blocked isocyanates. *Prog. Org. Coat.* 2001, 41, 1–83. [CrossRef]
14. Kothandaraman, H.; Nasar, A.S. The thermal dissociation of phenol-blocked toluene diisocyanate crosslinkers. *Polymer* 1993, 34, 610–615. [CrossRef]
15. Kawase, T.; Peng, X.; Ikeno, K.; Sawada, H. Surface modification of glass by oligomeric fluoroalkylating agents having oxime-blocked isocyanate groups. *J. Adhes. Sci. Technol.* 2001, 15, 1305–1322. [CrossRef]
16. Muramatsu, I.; Tanimoto, Y.; Kase, M.; Okoshi, N. Correlation between thermal dissociation and chemical structure of blocked isocyanates. *Prog. Org. Coat.* 1993, 22, 279–286. [CrossRef]
17. Wicks, D.A.; Wicks, Z.W., Jr. Blocked isocyanates III: Part A. Mechanisms and chemistry. *Prog. Org. Coat.* 1999, 36, 148–172. [CrossRef]
18. Rolph, M.S.; Markowska, A.L.J.; Warriner, C.N.; O’Reilly, R.K. Blocked isocyanates: From analytical and experimental considerations to non-polyurethane applications. *Polym. Chem.* 2016, 7, 7351–7364. [CrossRef]
19. Nasar, A.S.; Subramani, S.; Radhakrishnan, G. Synthesis and properties of imidazole-blocked diisocyanates. *Polym. Int.* 1999, 48, 614–620. [CrossRef]
20. Nasar, A.S.; Jaisankar, S.N.; Subramani, S.; Radhakrishnan, G. Synthesis and properties of imidazole-blocked toluene diisocyanates. *J. Macromol. Sci. Part A-Pure Appl. Chem.* 1997, 34, 1237–1247. [CrossRef]
21. Raab, W.P. Toxicology of the Imidazole Derivatives. In *The Treatment of Mycosis with Imidazole Derivative*, 1st ed.; Springer: Berlin, Germany, 1980; pp. 73–75.
22. Jung, J.C.; Park, S.-B. Synthesis and characterization of polyimides from imidazole-blocked 2,5-bis [(n-alkyloxy) methyl]-1, 4-benzene diisocyanates and pyromellitic dianhydride. *J. Polym. Sci. Pol. Chem.* 1996, 34, 357–365. [CrossRef]

23. Bae, J.-E.; Choi, J.-S.; Cho, K.S. An empirical model for the viscosity of reactive polymeric fluids. *Macromol. Res.* 2018, 26, 484–492. [CrossRef]

24. Maazouz, A.; Lamnawar, K.; Dkier, M. Chemorheological study and in-situ monitoring of PA6 anionic-ring polymerization for RTM processing control. *Compos. Part A Appl. Sci. Manuf.* 2018, 107, 235–247. [CrossRef]

25. Delebecq, E.; Pascault, J.-P.; Boutevin, B.; Ganachaud, F. On the versatility of urethane/urea bonds: Reversibility, blocked isocyanate, and non-isocyanate polyurethane. *Chem. Rev.* 2013, 113, 80–118. [CrossRef] [PubMed]

26. Cheikh, W.; Rozsa, Z.B.; Camacho Lopez, C.O.; Mizsey, P.; Viskolcz, B.; Szori, M.; Fejes, Z. Urethane formation with an excess of isocyanate or alcohol: Experimental and Ab initio study. *Polymers* 2019, 11, 1543. [CrossRef] [PubMed]

27. Jung, K.I.; Kim, B.; Lee, D.G.; Lee, T.-H.; Choi, S.Y.; Kim, J.C.; Noh, S.M.; Park, Y.I.; Jung, H.W. Characteristics of dual-curable blocked isocyanate with thermal radical initiator for low-temperature curing of automotive coatings. *Prog. Org. Coat.* 2018, 125, 160–166. [CrossRef]

28. Noh, S.M.; Lee, J.W.; Nam, J.H.; Byun, K.H.; Park, J.M.; Jung, H.W. Dual-curing behavior and scratch characteristics of hydroxyl functionalized urethane methacrylate oligomer for automotive clearcoats. *Prog. Org. Coat.* 2012, 74, 257–269. [CrossRef]

29. Oliver, W.C.; Pharr, G.M. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 1992, 7, 1564–1583. [CrossRef]

30. Hwang, J.W.; Kim, K.N.; Noh, S.M.; Jung, H.W. The effect of thermal radical initiator derived from O-imi-no-isourea on thermal curing characteristics and properties of automotive clearcoats. *J. Coat. Technol. Res.* 2015, 12, 177–186. [CrossRef]

31. Lee, D.G.; Sung, S.; Oh, D.G.; Park, Y.I.; Lee, S.-H.; Kim, J.C.; Noh, S.M.; Jung, H.W. Application of polycarbonate diol containing hindered urea to polyurethane-based clearcoats for tuning of scratch-healing properties. *J. Coat. Technol. Res.* 2020, 17, 963–976. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).