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Optimization of Mechanical Properties of Polyurethane/SiO_2 Nanocomposite on Polypropylene for Automotive Clear Coating by Taguchi Method

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ABSTRACT

The effect of different parameters including: nano silica content, curing temperature, type of hardener, and flash-off time on mechanical and optical properties of polyurethane (PU) based clearcoat was investigated via standard Taguchi L9 method. Dispersion of nano silica in the resultant nanocomposites was explored by scanning electron microscopy (SEM). SEM images showed a fine dispersion through the nanocomposites at different loadings. All PU nanocomposites showed gloss in the range of 91-94 which confirms that the presence of nano silica did not have an adverse impact on optical properties. Moreover, the most significant factor contributing to the hardness of the samples was the nano silica content. It was shown that high amount of nano silica (5 wt%) reduced the hardness of clearcoats due to interrupting curing process. The clearcoats performance after carwash test indeed showed that sample containing 2% nano silica cured at 85oC with a mixture of hardener (50% biuret, 50% trimer) after flash-off time of 5 min had the optimum physical and optical properties. Prog. Color Colorants Coat. 8 (2015), 295-307 © Institute for Color Science and Technology.

1. Introduction

Ensuring the exterior stability of automotive coatings, especially clearcoat layer, has been the center of attention in automobile industry since 1980s [1-3]. Generally, clearcoat layer, which is used for automobile glossy finishing, improves the physical and chemical properties of the automotive coating system. Despite exhibiting high gloss, clearcoats are suffering from different kind of damages caused during car washing or polishing with different equipment [4-8]. Furthermore, environmental circumstances may damage the surface of clearcoats during long time exposure. Therefore, to have a high quality clearcoat,

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prerequisite physical properties such as scratch resistance and hardness must meet relevant available standards. In other words, one can evaluate a clearcoat system performance according to their aforementioned physical properties [4-7].

One of the most widespread polymers used in clear coat systems is polyurethanes (PUs). Due to some drawbacks in physical and mechanical properties of PU, it is needed to modify PU by chemical and/or physical routes. Application of PU based composites containing different fillers such as montmorillonite [8], silica [6] and titanium dioxide [9] has been widely studied. It is proposed that by incorporating a high surface area of nanoparticle in polymeric matrix, its mechanical properties (i.e. scratch resistance, abrasion resistance and surface hardness) will be boosted as a result of changing chain dynamic around the interphase of nanoparticle/ polymer [5, 11, 12].

Moreover, by chemical crosslinking of PU based clearcoat, it has been shown that the physical properties of clearcoat are altered significantly. Also, the presence of nanoparticle in curing system would reduce the amount of chemical crosslinking which in turn lowers the glass transition temperature of composite resulting in an increase in clearcoat toughness [5, 6]. Rigidity of PU chain is another effective parameter on physical properties of PU coating that can be handled via controlling the type of hardener [20]. Considering physical and chemical methods for enhancing clearcoat performance, it is a prerequisite to control the amount of nano silica (A) as well as reaction parameters such as curing temperature (B), type of hardener (C) and flash-off time (D). Accordingly, design of experiments is of great importance to reduce number of experimental results to achieve the optimum condition for different variables.

Taguchi Method for design of experiments is based on a statistical approach in which variables are independent [8, 13]. Constructing orthogonal array to have an experimental design is straightforward and without any complications [14]. It is noteworthy to state that the result of applying the Taguchi method is a significant reduction in the number of experiments as well as selecting significant factors to make an optimization of the process studied.

To the best of our knowledge, there is no systematic investigation on experimental design of nano silica/ PU clearcoat system by means of Taguchi method. In this work, Taguchi method is applied for experimental design in order to explore the effect of different independent variables (A, B, C and D) on the synthesis of nano silica/ PU composite as well as the final clearcoat performance (qualitatively and quantitatively).

2. Experimental

2.1. Materials

Polyol and hardeners (DESMOPHEN A870) were supplied by Bayer Company. Detailed information is presented in Table 1. Moreover, METATIN 712 (DBTL company), OL17 (Berlocher company), and TINUVIN292 (Ciba Company) were used to provide good drying surface (hard dry), good leveling, and light stabilizer, respectively. Polysiloxane functionalized nano silica (NANOBYK3650) was purchased from BYK Company (Table 2). Butyl acetate and butyl glycol were provided from Merck. All materials were used as received.

Table 1: Physical properties of polyol and hardeners.

Name	Material	Viscosity at 23 °C (mPa·s)	NCO content[a]	NCO functionality
DESMOPHEN (A870 BAYER)	Hydroxyl gruppenhaltiges Polyacrylate	3500	------	------
DESMODUR (N75)	Aliphatic Polyisocyanate (HDI biuret)	225	16.5	3.8
DESMODUR (N3390)	Aliphatic Polyisocyanate (HDI Isocyanurate (Trimer))	550	19.6	3.5

[a] Weight percentage of free NCO groups, reported by supplier.

Table 2: General information of Nano silica.

Name	Nano particles	Nonvolatile matter	Nano particle content	Particle size (nm)	Liquid carrier
NANOBYK3650	Silica, surface modified with Polysiloxane (linear , non-polar)	31%	25%	20	Methoxy-propyl-acetate/Methoxy propanol 6/1

Table 3: Selected factors and levels.

Design parameter	Symbol	Level 1	Level 2	Level 3
Nano silica (weight %)	A	0	2	5
Curing temperature (^oC)	B	70	80	85
Hardener	C	Biort	Trimer	50% Biort, 50% Trimer
Flash-off time (min)	D	5	12	15

Table 4: Standard L9 orthogonal array for factors and levels in this study.

Run	A	B	C	D
1	0	70	Biort	5
2	0	80	Trimer	12
3	0	85	50% Biort, 50% Trimer	15
4	2	70	Trimer	15
5	2	80	50% Biort, 50% Trimer	5
6	2	85	Biort	12
7	5	70	50% Biort, 50% Trimer	12
8	5	80	Biort	15
9	5	85	Trimer	5

2.2. Design of experiments

The factors in this study were the percentage of nano silica, curing temperature, type of hardeners, and flash-off time as detailed in Table 3. According to Taguchi method, a standard L_9 orthogonal array was selected (Table 4). Based on the accepted approach in applying different runs to eliminate the probable systematic bias, randomized selection of runs was carried out [8].

2.3. Preparation of PU/nano silica clearcoat

In the first step, polyol and nano silica were mixed together under 1000 rpm stirring for 20-25 min at room temperature. Then, appropriate amount of hardener (with the mass ratio of 30:70 with respect to polyol) was mixed into the slurry. The resultant slurry was sprayed to fabricate clearcoat film on different cleaned substrates (Polypropylene and aluminum substrate was employed according to standard). In the next step, flash-off time was considered to evaporate solvent from applied film. Finally, samples to be cured in oven for 20 min.

2.4. Characterization

In order to study the morphology of samples, scanning electron microscopy (SEM) was utilized under 15 kV (Vega-Tescan, Germany). To investigate optical properties of clearcoat systems, we used a BYK-Gardner Micro-Tri glossmeter (Germany) according to ASTM D523 and D2457. The adhesion properties of clearcoat systems were measured by cross hatch cut method according to ASTM D3359-2. To determine hardness, pendulum hardness tester (BYK Gardner Company) was used according to ASTM D4366. To simulate carwash condition according to the PSA D245359/c/2033 (Peugeot standard) carwash simulator was employed (Pars Horm Co, IRAN). A carwash simulator having polyethylene brush type, 318–320 nm brush length, washing powder of Al_2O_3 (suspension), flow rate of 2 drop/min, and car wash rotating speed of 150 rpm was used to produce scratches on the clearcoat system applied on the substrate. The durability in a carwash test was measured in terms of gloss retention. Specular gloss at an angle of 20^{o}C was measured using a BYK-Gardner Micro-Tri Gloss gloss meter (Germany).

3. Results and discussion

3.1. Dispersion state of nanocomposites

One of the most challenging concepts in incorporating nanoparticle into polymeric matrix is the state of dispersion. SEM images were provided to investigate how much nanoparticles are dispersed. As it can be seen from Figure 1, nano silica powders in all samples were finely dispersed during nanocomposite preparation. The spherical morphology of nano silica was obtained in all samples. The average diameter was measured to be around 40 nm ±15 nm. This confirms that the aggregation of nanoparticles did not occur in the samples during nanocomposites preparation.

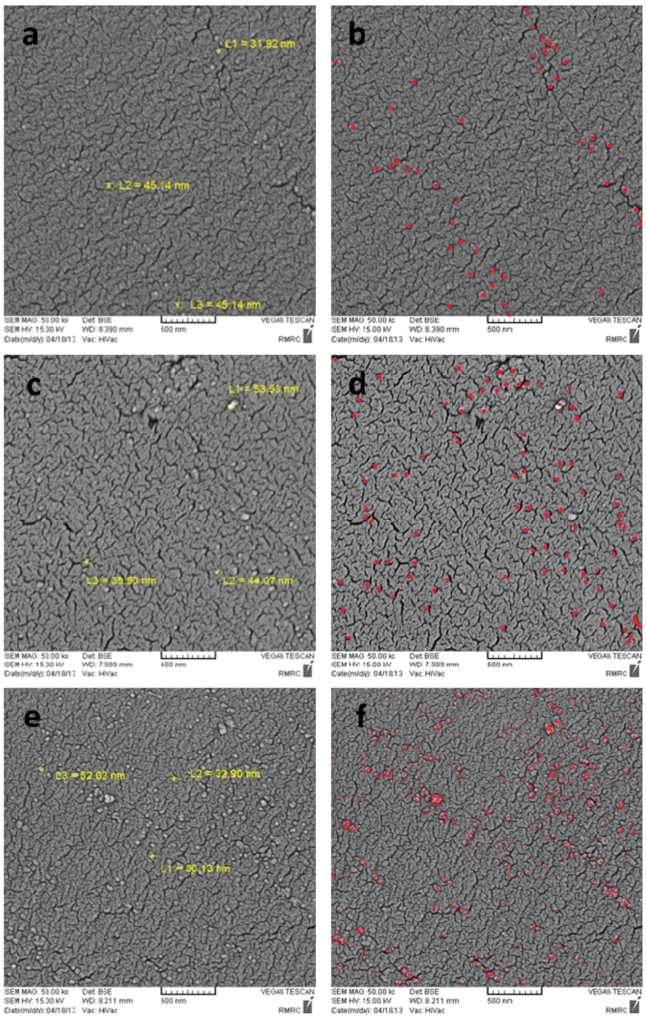

Figure 1: SEM images of nanocomposites of (a) sample 5, (c) sample 6, (e) sample 9. EDX of (b) sample 5, (d) sample 6, (f) sample 9.

To analysis the data obtained from Taguchi method, analysis of variance (ANOVA) was considered to illustrate how much a factor is effective on the results of experiment by comparing each factor's variation to the total calculated variation [14]. Qualitek-4 (Nutek Inc.) software was utilized for the statistical analysis. More specifically, for two types of experiments carried out in this work, namely gloss and hardness, the ANOVA terms had been calculated. To explore and determine the effective factors and the effectiveness of each factor, F-ratio and percent contribution are suitable criteria [14].

3.2. Characterization of the films before car-wash

3.2.1. Gloss

Gloss of a coating can be correlated with different variables such as surface roughness, aggregation of nanoparticles, miscibility of resin and hardener, and so on. In the range studied here. There is no significant difference in gloss of samples before carwash (Figure 2). In fact, by considering the experimental error (2 units), the results are almost in the same order. This finding is important from a technological point of view. In other words, it means that introducing silica nanoparticles in the PU matrix did not change gloss compared to neat PU. Also, the ANOVA (Table 5) for gloss test indicates that the error/other term, including uncontrollable factors, factors that are not considered in the experiments, and the experimental error, is more significant compared to A, B, C, and D factors. This finding means that none of the selected factors are important in the samples' gloss results.

As it was indicated in Figure 1, the nano silica diameter in the nanocomposite did not exceed 50 nm as a result of fine dispersion of nanoparticles in the PU matrix. Therefore, particle size of nano silica is smaller than the wavelength of visible light. This is the basic reason for retaining the high value of gloss for all samples studied, even the ones with 5wt% nano silica loading.

3.2.2. Hardness

From F-ratio, it can be interpreted that two factors, namely nano silica content and type of hardener, can control hardness of nanocomposite (Table 6). Moreover, the effect of nano silica content on hardness of PU nanocomposites has the most prominent impact, as can be seen from percent contribution value in Table 6. The other important conclusion from the obtained results is that curing temperature and flash-off time have no significant influence on hardness properties. It should be taken into account that these results are valid for the ranges studied here.

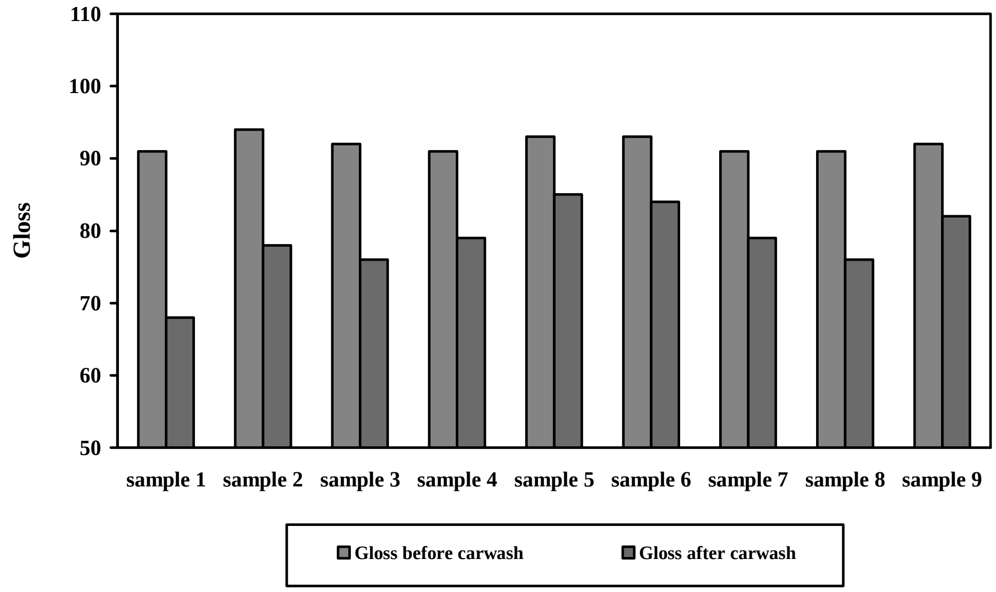

Figure 2: Gloss of different samples before and after carwash.

Table 5: ANOVA table for gloss before carwash.

Factors	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F-Ratio (F)	Pure Sum (SS)	Percent P (%)
A	2	6.012	3.006	3.008	4.014	8.362
B	2	13.999	6.999	7.004	12.001	25.002
C	2	2	1	1	0.001	0.002
D	2	7.999	3.999	4.002	6.001	12.502
Other / Error	18	17.987	0.999	-	-	54.132
Total	26	48				100.00%

Table 6: ANOVA table for hardness before carwash.

Column / Factors	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F-Ratio (F)	Pure Sum (SS)	Percent P(%)
A	2	1234.692	617.346	213.963	1228.922	79.973
B	2	4.692	2.346	0.813	0	0
C	2	204.654	102.327	35.465	198.883	12.942
D	2	40.692	20.346	7.051	34.921	2.272
Other / Error	18	51.934	2.885	-	-	4.813
Total	26	1536.666				100.00%

The hardness obtained for different samples are depicted in Figure 3. As it is demonstrated in this Figureure, a bell curve behavior is observed which implies that there is a competition between two opposing parameters.

3.2.3. Effect of nano silica content

In order to better illustrate the trend of variation of each factor, main-effect plots are presented in Figure 4. The hardness of a given polymeric nanocomposite is mainly affected by two parameters, crosslinking density (CLD) and the presence of high hardness fillers. Both factors have a similar behavior on hardness; by increasing CLD and/or filler content, the hardness of sample increases correspondingly. However, another possibility for reduction of hardness arises from the interrelated role of nano silica on CLD and hardness. It has been reported that nano silica will act as an obstacle for PU resin to be cured. Therefore, by increasing nano silica in the reaction medium, the amount of junctions that connect resin chains together is reduced. As a result, one can deduce that the presence of nano silica leads to CLD decrease.

Addition of nano silica to the PU matix will increase its hardness up to 2wt%. The possible reason for this phenomenon is that the presence of nano silica will not affect CLD significantly, while its impact on hardness is important. However, when the amount of nano silica is increased to 5wt%, CLD will be decreased in such a way that compensates the role of nano silica as a reinforcing agent. Schematic representation of the effect of nano silica on CLD is shown in Figure 5.

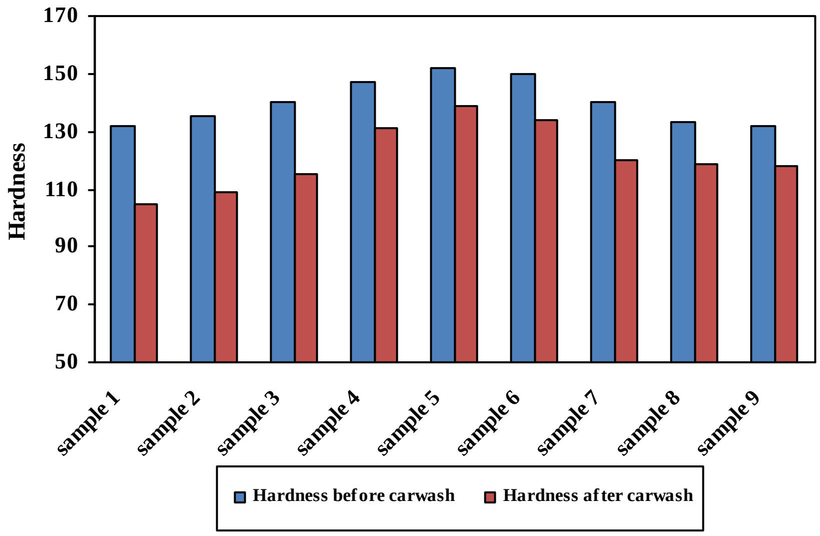

Figure 3: Hardness of different samples before and after carwash.

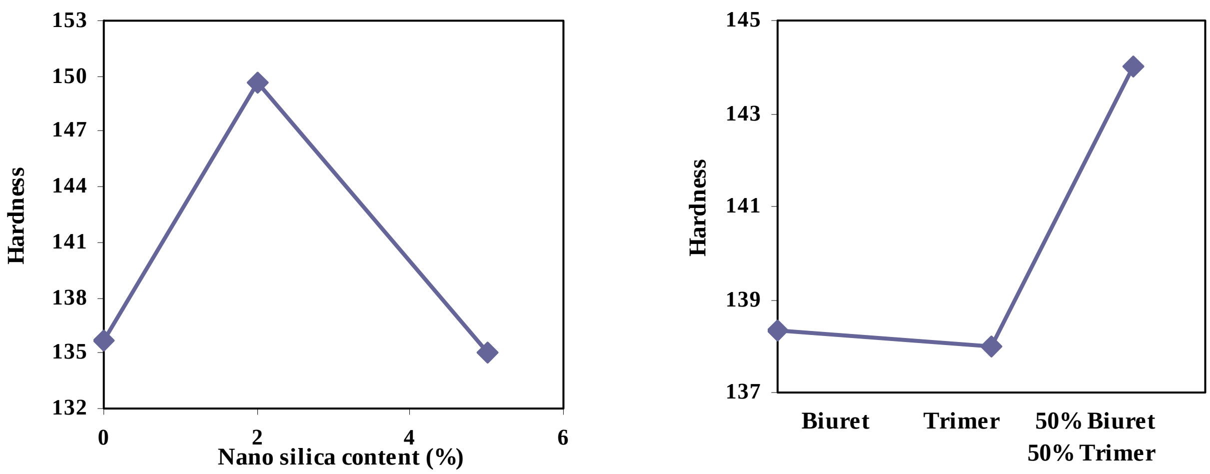

Figure 4: Main effect of (a) silica content, (b) type of hardener on hardness of samples before carwash.

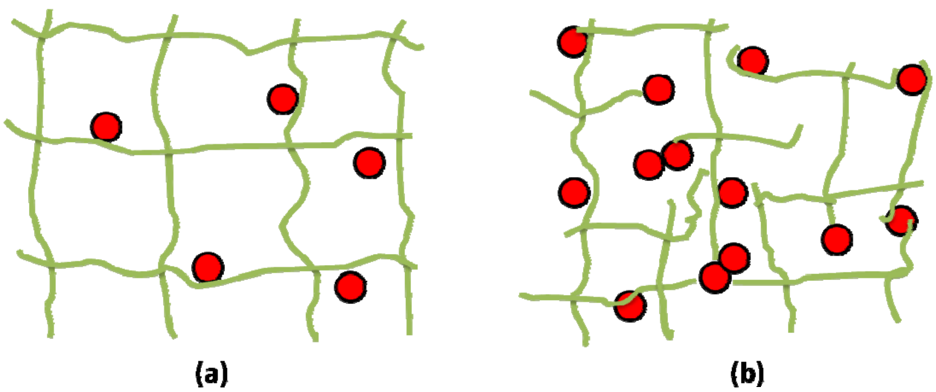

Figure 5: Schematic representation of nanocomposites containing (a) 2wt% nano silica, and (b) 5wt% nano silica.

3.2.4. Effect of type of hardener

The second important factor that plays a key role in controlling hardness of nanocomposites is the type of hardener. As it can be realized from Figure 4b, incorporating of biuret or trimer did not change hardness of nanocomposite significantly. On the other hand, when both of these hardeners were simultaneously utilized for curing, substantial improvement in hardness was achieved.

Molecular structure of hardeners used in this study can be found in Figure 6. Due to the absence of ring in backbone of biuret hardener, the ability of branches for molecular movements makes it possible for chains to entangle which may restrain the full crosslinking capacity. On the other hands, trimer hardener has a ring inside the backbone which possesses a more stiffer structure than biuret. Therefore, the growing chains are less able to associate in the curing process. As a result, the amount of crosslinking in this case would be low which leads to low measured hardness. However, when both hardeners are used for curing process, a synergy is observed. To explain relatively high hardness obtained for sample containing 50% biuret and 50% trimer, it can be suggested that the relative movement of chains is regulated to slow down the chains entanglement on the one hand, and the curing process is fast enough to satisfy high CLD, on the other hand [15].

3.3. Characterization of the films after carwash

3.3.1. Gloss

From technical points of view, it is desirable to maintain the physical properties of clearcoat as close as possible to the pristine properties before carwash. To evaluate final physical properties of clearcoat, gloss was measured in comparison with data obtained before carwash (Figure 2). ANOVA table for gloss after carwash is available in Table 7. In this case, from percent contribution it can be understood that the main significant factors have been considered properly, as the contribution of other/error terms is almost insignificant. There are three factors which are important in determining gloss value after carwash, namely nano silica content, curing temperature, and type of hardener (Table 7).

From main plots, it is convenient to deduce the effect of each factor separately. During carwash, one of the most important damages, i.e. scratch, can change the appearance of clearcoat significantly. It is reported that scratch is mainly responsible for causing damage in a clearcoat [6, 17]. Therefore, to maintain the highest values of a clearcoat's gloss, it is necessary to optimize its mechanical properties under different types of forces during carwash procedure [16, 17, 18]. In other words, the higher the mechanical properties (high scratch resistance), the higher the amount of gloss retention after carwash. Since there is a relationship between scratch resistance and hardness, we used hardness to evaluate sample's scratch resistance [20].

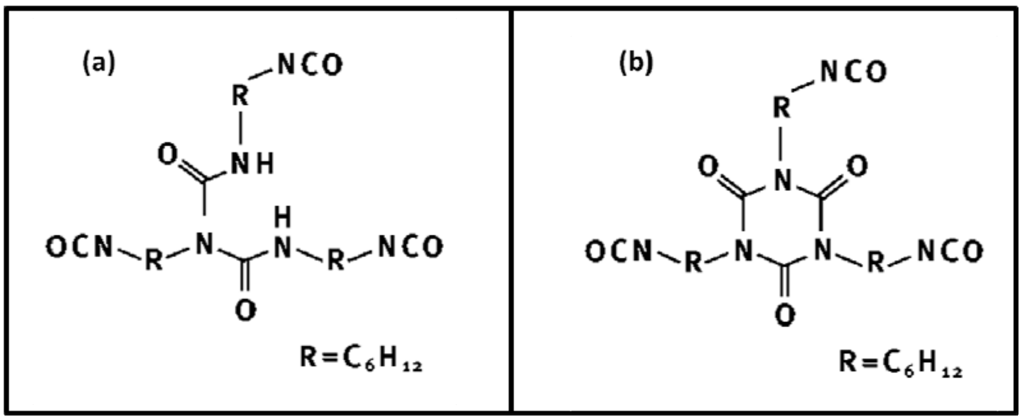

Figure 6: Chemical structure of (a) Biuret, and (b) Trimer.

Table 7: ANOVA table for gloss after carwash.

Column / Factors	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F-Ratio (F)	Pure Sum (SS)	Percent P (%)
A	2	340.662	170.331	85.156	336.662	50.957
B	2	144.662	72.331	36.161	140.662	21.29
C	2	88.663	44.331	22.163	84.662	12.814
D	2	50.673	25.336	12.667	46.673	7.064
Other / Error	18	36.003	2	-	-	7.875
Total	26	660.666				100.00%

3.3.2. Effect of nano silica content

In Figure 7a, there is an optimum for nano silica content to attain maximum gloss after carwash. It is believed that one possible mechanism to reduce scratch during carwash is slippage mechanism induced by nano silica [5, 19]. In fact, surface migration of nano silica during curing process due to distinct surface energy from bulk, may help scratch resistance of nanocomposite [19]. As nano silica content is increased up to 2wt%, one can expect that gloss retention should be better as a result of higher hardness at this nano silica content. As it was discussed previously, this increment can be simultaneously related to the effect of nano silica presence in the nanocomposite and negligible loss of CLD. When the amount of nano silica is increased to 5wt%, the CLD loss would be high enough to easily scratch the nanocomposite. Consequently, the formed scratches during carwash results in higher surface roughness which in turn leads to lower gloss measured after carwash.

3.3.3. Effect of curing temperature

The effect of curing temperature on gloss after carwash can be associated with the formation of polymeric network during crosslinking which subsequently influences the CLD of the system (Figure 7b). According to the Arrhenius equation, the rate constant of polycondensation reaction between isocyanate and polyol is increased by temperature [20]. Thus, it is expected that the amount of CLD would be enhanced. However, there is a small amount of hardness increase when temperature is increased from 80^{o}C to 85^{o}C. This may be attributed to a parallel reaction taking place to produce tertiary amine (branching) [20].

3.3.4. Effect of type of hardener

Type of hardener plays a minor role in determining gloss retention after carwash. The combination of both hardeners creates a better network which is able to resist against scratches caused during carwash (Figure 7)

3.3.5. Hardness

In order to evaluate the mechanical properties of samples after carwash, hardness test was carried out which is presented in Figure 3. Analogous to data obtained before carwash, a bell curve can be realized which demonstrates a competition between two opposing parameters. ANOVA table for hardness after carwash is also depicted in Table 8.

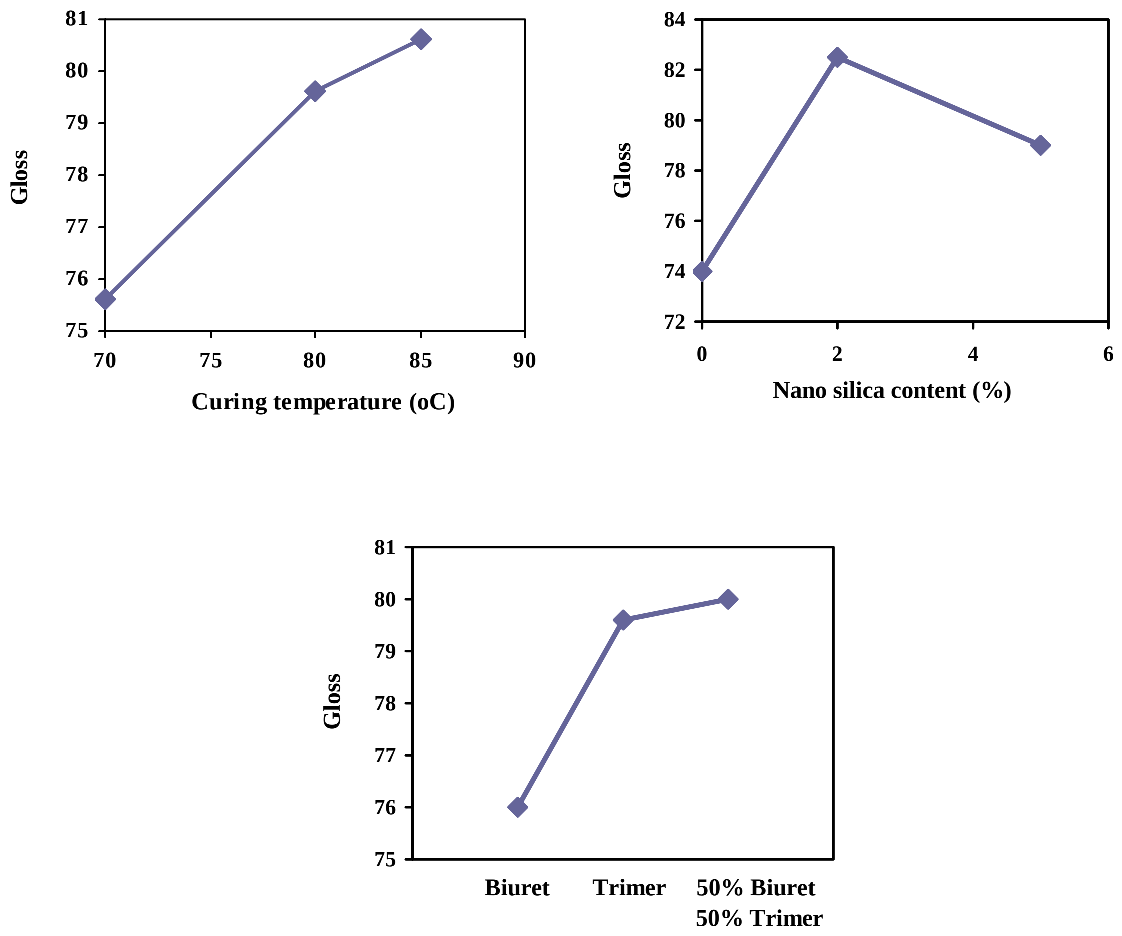

Figure 7: Main effect of (a) nano silica content, (b) curing temperature, and (c) type of hardener on gloss of samples after carwash.

Table 8: ANOVA table for hardness after carwash.

Factors	DOF (f)	Sum of Sqrs. (S)	Variance (V)	F-Ratio (F)	Pure Sum (SS)	Percent P (%)
A	2	2872.673	1436.336	300.653	2863.119	89.064
B	2	80.672	40.336	8.443	71.117	2.212
C	2	170.671	85.335	17.862	161.117	5.011
D	2	4.655	2.327	0.487	0	0
Other / Error	18	85.992	4.777	-	-	3.713
Total	26	3214.666				100.00%

As it is obvious from this table, main contributor to hardness after carwash is nano silica content which has a percent contribution of almost 90%. These data are in accordance with hardness before carwash. The main difference arises between data before and after carwash is the lack of contribution of type of hardener to hardness after carwash. It should be taken into account that the effect of factors with less than 10% contribution of the highest contributor will be considered as error terms [14].

From main plot of hardness after carwash it can be seen that by increasing nano silica content up to 2%, there is an improvement in hardness of samples. When it is raised to 5%, a drop can be found in hardness (Figure 8). Again, this behavior can be related to the interconnected role of nano silica and CLD.

3.3.6. Optimum condition

In order to determine the optimum conditions for producing a clearcoat with superior final optical and mechanical properties, main-plots of gloss and hardness after carwash were employed. In this regards, different factors should be set as shown in Table 9. It is worth to note that because flash-off time did not affect gloss and hardness significantly, the economic condition was considered to select the optimum level for this factor.

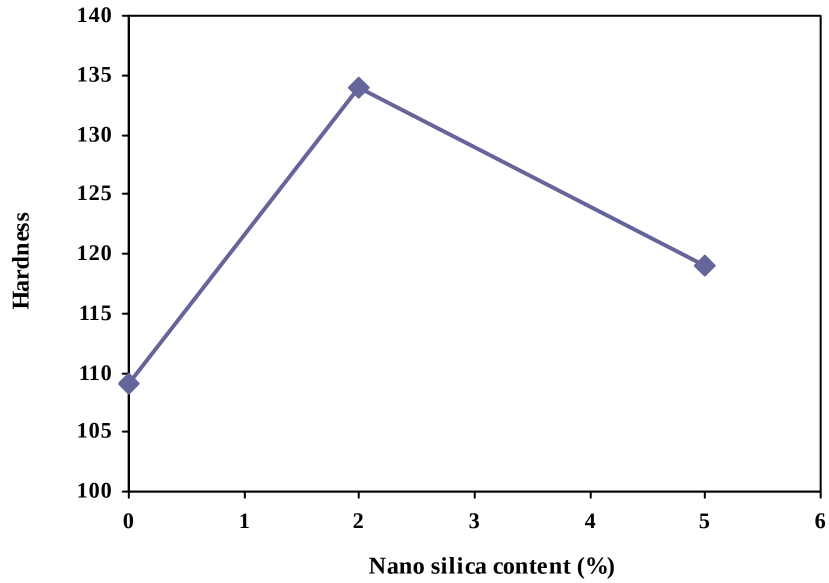

Figure 8: Main plot of hardness after carwash.

Table 9: Optimum condition of design parameter obtained in this study.

Design parameter	Symbol	Optimum level	Value
Nano silica (weight %)	A	2	2
Curing temperature (^oC)	B	3	85
Type of hardener	C	3	50% Biort, 50% Trimer
Flash-off time (min)	D	1	5

4. Conclusions

In this study, the effect of different design parameters including nano silica content, curing temperature, type of hardener, and flash-off time on mechanical and optical properties of PU based clearcoat before and after carwash was investigated via standard Taguchi L_9 method. Gloss of all samples before carwash was in the range of 91-94. Hardness of samples was affected by nano silica content (~80% contribution) and type of hardener (~13% contribution) before carwash. Nano silica content played the key role in determining hardness before and after carwash. Gloss retention of samples was affected by nano silica content (~50% contribution), curing temperature (~21% contribution), and type of hardener (~12% contribution) after carwash. Optimum condition of design parameter to have a maximum optical and physical properties was considered as: nano silica content (2 wt%), curing temperature (85 ^{o}C), type of hardener (50% biuret and 50% trimer), and flash-off time (5 min).

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