Macromolecular Nanotechnology

Tribological properties and scratch healing of a typical automotive nano clearcoat modified by a polyhedral oligomeric silsesquioxane compound

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\textbf{Article Info}

\textbf{Article history:}
Received 18 June 2014
Received in revised form 24 August 2014
Accepted 27 August 2014
Available online 7 September 2014

\textbf{Keywords:}
Automotive clearcoats
Scratch resistance
Polyhedral oligomeric silsesquioxane nano-structures (POSS)
Healing
Thermo-mechanical properties

\textbf{Abstract}

The present work has studied the influence of an OH-functionalized polyhedral oligomeric silsesquioxane(POSS) nano-structure on the scratch resistance of a typical acrylic melamine clearcoat. Scratch resistance and the healing ability of clearcoats were investigated by micro-scratch studies and confocal profilometry techniques. In addition, hardness and thermo-mechanical characteristics of clearcoats were investigated by micro-indentation and dynamic mechanical thermal analysis (DMTA) respectively, to correlate the scratch behavior to the mechanical and structural properties of the clearcoats. The results revealed that incorporation of POSS cages into clearcoats could effectively enhance the scratch resistance. This was attributed to the higher hardness and cross-linking density of the resulting nanocomposite coatings. The healing results also demonstrated that nanocomposites had a higher healing ability compared to the neat clearcoat. The higher healing of nanocomposites was explained by the physical H-bonding interactions formed in vicinity of POSS cages. The transparency measurements proved that these improvements were fulfilled without any negative effect on the optical quality of clearcoats.

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1. Introduction

Appearance is an important factor affecting the overall quality and acceptability of a car from customer’s view. This is why coating scientists have been trying to develop formulations with enhanced properties. Use of basecoat/clearcoat instead of conventional mono-layer topcoats, high gloss clearcoats, and incorporation of pearlescent pigments in basecoats are examples of such attempts. In these approaches, maintaining the appearance is very crucial.

Scratches and mar are the most important factors damaging the coating films [1]. Improved scratch resistance of the automotive coatings is the main target in this regard [2,3]. Resistance against scratch, results in protection of coating film being mechanically damaged upon exposure to environmental factors [4]. The scratch resistance of a coating can be enhanced through one or combination of the following approaches [5–10]: increase in hardness (hard enough for objects to penetrate into the coating), decrease in friction coefficient (slippery surfaces) or increase in elasticity–toughness. The latter makes the surface to resist further penetration and shows capability to recover to its original form. Surface additives such as those based on silicone compounds are those amongst earlier studies for such purposes [11,12]. Being unable to significantly improve the scratch behavior and also due to the fact that these are easily wiped out from the surface have
Prepared them to be universally accepted. Scientists have paid many attentions to the novel methods based on nanotechnology during recent decades. Nano-scale particles having a high surface area which significantly enhance the particle surface–matrix interactions can considerably reinforce the network against mechanical deformations [13, 14]. Development based on these methods has resulted in considerable improvement in mechanical and tribological properties of coatings [15]. It has been revealed that some particles like silica, alumina and zirconia can increase the scratch resistance of the clearcoats while maintaining the transparency of the clearcoat unaffected [15–17]. High surface area of these inorganic particles renders them to aggregate and makes their dispersion in organic binders difficult. To overcome this problem, changes in the nature of the particles surface are possible. Some hybrid materials like silane-based compounds have been employed to tune the surface chemistry of inorganic particles to an organic/inorganic (hybrid) structure by which the affinity and dispersion of nanoparticles into organic matrices can be enhanced [18, 19]. It has also been demonstrated that those surface treated particles covalently link the particle to the matrix and create higher level of reinforcement [20]. Alternatively, the growth of nanoscale domains in an organic media via in-situ sol–gel reactions is a promising method for scratch resistance enhancement [21]. These latter approaches (sol–gel processing and use of particles) have both inherent difficulties.

Polymethacrylic silsesquioxane compounds are the most recent materials which have been used to enhance the mechanical properties of polymers [22]. Their cubic structure consisting of a core based on Si–O–Si and several organic groups on the corners have given these structures numerous advantages. Their size (1–3 nm depending on their organic side groups), their monodisperse and molecule-like behavior make them soluble in the media. The presence of several organic groups on each corner facilitates their dispersion into organic media like polymers and binders [23–25]. In addition, proper selection of the polyhedral oligomeric silsesquioxane compound with respect to the matrix in which it is dispersed makes it capable of covalently linking to the matrix. It has been demonstrated that the chemical bonding between the filler and the matrix create a reinforcing effect and it would intensify this effect if the filler is attached to the matrix at more than one corner [26]. These attractive properties have made these novel compounds as promising candidates to be used for a wide range of applications in polymers as thermal resistant [27, 28], fire retardant [29, 30], water repellent [31, 32], anti-bacterial [33, 34] and particularly as reinforcing agents [35–40]. In a recent study, polyhedral oligomeric silsesquioxane nano-structures possessing methacrylate functionalities were incorporated into a UV-cured ethoxyolated dimethacrylate resin [22]. Their results revealed that the addition of these nano-structures could significantly improve the scratch resistance.

This work attempts to study the capability of using a polyhedral oligomeric silsesquioxane nano-structure to improve the scratch resistance of automotive clearcoats. The clearcoat employed was a typical one based on OH-functional acrylic resins to be cured with a melamine cross-linker. Polyhedral oligomeric silsesquioxane nano-structures used was also OH-functional. The clearcoat formulation was modified in such a manner to partially replace the OH-functionals of acrylic resin with those of nanostructure POSS. The scratch behavior and healing ability of modified clearcoats were comprehensively studied using progressive scratch testing, hardness and thermal healing. The scratch behaviors were finally correlated to some structural properties of nanocomposites.

2. Experimental

Acrylic resin (Tacryl 765ZA, Mw = 13000 g/mol, with a hydroxyl content of 4.2%) and partially butylated melamine resin (Tasmine 564 N) were supplied by TAAK Resin Co. (Iran). A weight ratio of 70:30 (acrylic: melamine) was considered as the basis of formulation. A hydroxyl-functional polyhedral oligomeric silsesquioxane (POSS), AL-0136 which was based on octa (3-hydroxy 3-methyl butyl dimethyl siloxy) structure, procured from Hybrid Plastic Inc., was employed to partially substitute the hydroxyl functional groups of acrylic resin. The general structures of acrylic, melamine and POSS are presented in Fig. 1. POSS was added to the acrylic/melamine clearcoat formulations in such a manner that replace 0%, 5%, 10%, 15% and 25% of OH functional groups of acrylic in the formulations. POSSX represents the clearcoat formulation in presence of POSS where “X” denotes the mol percentage of POSS in the formulation and varies from 0 to 25. POSS was dissolved in butyl acetate and then was added to the acrylic/melamine solution. Table 1 lists the ingredients used in each modified clearcoat.

Some additives including acid catalyst (1.5 wt.% of total formulation, para-toluene sulfonic acid, PTSA) and a defoamer (0.2 wt.% of total formulation, Delta-FC 1040) were also added to the clearcoat formulations. All formulations were then mixed for 60 min using a high shear stirrer. The liquid formulations were quite transparent. The modified clearcoats were applied on pre-cleaned glass substrates. Samples were then cured at 140 °C for 25 min. The thickness of cured films was 65 ± 5 μm. Free films were also prepared by immersing the glass coated substrates in water and removing after 5 min.

2.1. Characterization

The micro-scratch tests were carried out using a Rockwell indenter (tip radius = 800 μm) mounted on a CSM Micro-Combi tester instrument. The scratch test was conducted via a three-stage mode: pre-scan, scratching and post-scan. First, the indenter applied a low load (20 mN) on the surface to record the surface profile (pre-scan). For scratching, a progressive normal force from 20 up to 30,000 mN at a constant rate (around 4996 mN/min) was applied to the clearcoat surface and 6 mm-long scratches were made at a rate of 1 mm/min. Finally, the indenter applied a low load (20 mN) on the scratched surface to record the surface profile after scratch and after elastic recovery (post-scan). The three-stage process was replicated 3 times for each sample. The resultant scratches
were studied directly by the aid of an optical microscope to find the position of first and second (if any) critical forces (abbreviated as FCF and SCF respectively). FCF is the force at which the scratch trace becomes visible and SCF is the lowest force which causes coating rupture.

The effects of POSS addition on the cross-linking density and glass transition temperature ($T_g$) were studied by means of a Q800 DMTA (TA instruments). Experiments were carried out in a tension mode on free films at 1 Hz. The heating range was 25–200 °C and the heating rate was 5 °C/min (according to ASTM E1640-04). Cross-linking density was calculated from rubbery plateau zone of storage modulus ($\hat{\epsilon} = E/3RT$) where $\hat{\epsilon}$ is cross-linking density and $R$ is gas constant. $E$ and $T$ are storage modulus and temperature at the initial point of rubbery zone, respectively.

Micro hardness of the clearcoats containing various loads of POSS was determined using a Leica VMHTMOT micro-indenter equipped with a Berkovich diamond tip (3-faced pyramid) according to the following equation:

$$H = 1854.4 \times \frac{P}{d^2}$$

where $H$ is hardness, $P$ is the applied load and $d$ is the diagonal Vickers indentation. A normal force of 19.6 N was applied for 15 s.

After scratch test, the profile of the scratched surface was recorded by confocal profilometry (Conscan profilometer, CSM Instruments) which had been mounted and attached to the scratch test device as an accessory. After recording scratch data, the scratched surfaces of various clearcoats were subjected to a thermal healing process. The samples were kept at 100 °C for around 8 h. This temperature was chosen because it was near the glass transition temperature of clearcoats. After the healing process, the samples were again mounted on the scratching machine (exactly on the position of the healed scratches) to conduct a scratch run (only pre-scan to take image). The profilometry technique was also used to record the profile of healed scratches.

In order to detect variations in intermolecular interactions such as hydrogen bonding in presence of POSS nanocages, FTIR spectroscopy was employed. A Perkin Elmer Spectrum™ One FTIR Spectrometer model IFS48 was utilized. Transparency of clearcoat free films was measured using a Cary100scan UV–Visible spectrometer (Varian Company) in transmission mode in the range of 200–700 nm.
3. Results and discussion

3.1. Scratching behavior

As stated earlier, the main purpose of introducing POSS nanostructures into automotive clearcoats is enhancing their scratch resistance. Scratching behavior of the blank and all POSS-containing clearcoats was investigated by means of a scratch tester. An optical microscope with magnification of $5 \times$ was used to find the position of critical load. Fig. 2 depicts the optical images of all clearcoat surfaces after scratch testing.

General overview of Fig. 2 reveals that incorporation of POSS nanostructure into clearcoat enhances its resistance against scratch but this is accompanied by the occurrence of some rupture at high applied forces. FCF and SCF evidences can be utilized to quantify the variations in scratch behavior of clearcoats containing various loadings of POSS nanostructures. The scratch behavior is quantified in terms of critical applied normal forces. Due to the importance of visual aspect of scratches, the force producing a visible deformation on the surface can be considered as a quantitative criterion for scratch resistance. Therefore, the FCF value of clearcoats was regarded as the scratch resistance [6]. In addition, occurrence of any rupture during scratching can reflect the maximum endurance of clearcoat against applied force beyond which the coating is torn [6]. The SCF value reflects the ductility of the coating. The critical loads for all clearcoats are listed in Table 2.

As clearly seen in Fig. 2 and Table 2, it is obvious that addition of POSS into clearcoat increases its scratch resistance. As the POSS content increases (up to POSS15 sample), the FCF (scratch resistance) shifts to higher values. In case of POSS25, the scratch resistance slightly decreases. An improvement around two fold was achieved by addition of only 6 wt.% of POSS structures. In case of SCF, while the pristine clearcoat does not experience any rupture in the whole range of measurements (0–30 N), the nanocomposite coatings are torn at different forces. As the POSS content increases, the SCF values shifts to lower forces indicating the less ductility of nanocomposites. These results reveal that although POSS considerably enhances the scratch resistance, it increases brittleness. It would increase the chance of the creation of undesired fracture scratches if the surface is abraded by abrasive objects like tree branches or carwash brushes.

Elastic recovery in scratch test is assigned to the ability of coating to get back (return) to its original state (position) immediately after being deformed by the indenter [7,41]. It is calculated by dividing the residual depth to the penetration depth. Elastic recovery values at 1 and 15 N were calculated and presented in Table 2. Low and high forces were considered to respectively characterize the surface and bulk of the coatings. Recovery values at 1 N reveal that in spite of slight fluctuations, elastic recovery increases as the POSS content increases. In case of 15 N, elastic recovery regularly increases to a certain amount after which elastic recovery slightly diminishes. These results prove that POSS nanostructure enhances the elasticity in both surface and bulk of coating. It demonstrates that elasticity enhancement is one of the possible mechanisms of scratch resistance improvement.

3.2. Hardness

In order to find out the reason of scratch resistance improvement caused by POSS incorporation, hardness of samples were measured by micro-hardness testing. Micro-hardness results of different clearcoats are depicted in Fig. 3.

As clearly seen in Fig. 3, the hardness increases as 15% of hydroxyl groups are replaced by those of POSS. For higher loadings of POSS, hardness value slightly decreases. The variation trend of micro-hardness and scratching data

Fig. 2. Optical images of scratched surfaces of various clearcoats loaded with different contents of POSS nanostructure.
seems similar and the possibility of linear correlation was investigated. These correlations are presented in Fig. 4.

Diagrams in Fig. 4 clearly indicate a good correlation between micro-hardness and FCF or SCF values. The higher hardness shows higher scratch resistance. It is logical because a hard surface impedes coating deformation and thus indenter penetrates less into the coating. Therefore, increase in hardness could be another mechanism involved in the scratch resistance improvement of clearcoats containing various loads of POSS. In addition, it is seen that the harder the coating is, the lower SCF value it has. This demonstrates that increase in hardness causes the coating to become a more brittle object. The lower correlation coefficient of micro-hardness and FCF may be due to the influence of other factors such as frictional coefficient and elastic recovery that affect the FCF.

3.3. Healing

While different strategies such as increase in hardness, toughness–elasticity, and slipping properties of the coating could be employed to prevent from or decrease the chance of mar and scratches formation, there could be still a chance to heal the scratches which have been formed on the coating. Healing of the scratches may be the last opportunity to fight against the spoiling effect of scratches.

Table 2
First, second critical forces and elastic recovery values at 1 and 15 N of different clearcoats.

<table>
<thead>
<tr>
<th>Sample</th>
<th>POSS0</th>
<th>POSS5</th>
<th>POSS10</th>
<th>POSS15</th>
<th>POSS25</th>
</tr>
</thead>
<tbody>
<tr>
<td>First critical force (N)</td>
<td>2.37 ± 0.20</td>
<td>3.81 ± 0.64</td>
<td>4.15 ± 0.13</td>
<td>4.47 ± 0.32</td>
<td>4.20 ± 0.63</td>
</tr>
<tr>
<td>Second critical force (N)</td>
<td>Not seen</td>
<td>28.49 ± 1.25</td>
<td>28.96 ± 0.45</td>
<td>18.97 ± 1.22</td>
<td>23.82 ± 0.93</td>
</tr>
<tr>
<td>Elastic recovery at 1 N (%)</td>
<td>98.7 ± 0.7</td>
<td>98.3 ± 0.5</td>
<td>97.9 ± 0.4</td>
<td>99.8 ± 0.2</td>
<td>100 ± 0.20</td>
</tr>
<tr>
<td>Elastic recovery at 15 N (%)</td>
<td>81.2 ± 0.8</td>
<td>83.9 ± 0.7</td>
<td>83.6 ± 0.4</td>
<td>91.7 ± 1.1</td>
<td>87.6 ± 0.8</td>
</tr>
</tbody>
</table>

Fig. 3. Micro-hardness results of different clearcoats.

Fig. 4. Correlation between scratch and microhardness data.
ability of different nano-structured coatings to heal the scratches formed on their surface was investigated after being exposed to a thermal healing process. The optical images of scratched surfaces after healing process are presented in Fig. 5.

The healing ability of coatings can be judged based on the healing of the main trace of the scratch and the healing of the various ruptures produced during scratching. Comparison of the optical images of scratched and healed areas (Figs. 2 and 5) reveal that for all clearcoats the scratch grooves have been relatively disappeared and it seems that the surface has returned in great extent to its initial position. This can be indicative of an inherently good healing ability of acrylic/partially butylated melamine systems which may be attributed to the polar structure of melamine-based scaffold. It is well known that development of non-covalent interactions like ionic, polar and hydrogen bonding are of the most important mechanisms involved in the enhancement of healing ability of coatings [42–46]. It is due to the thermal reversibility of these interactions which provide this chance for polymeric chains to easily move and re-arrange during a thermal healing process. Numerous polar sites for physical and hydrogen bonding interactions have made melamine attractive to scientists to employ this structure for the applications where non-covalent interactions are desired (i.e. in the field of supramolecules [47,48]). Although melamine is used as covalent cross-linker in most of thermosetting systems and is not free enough to behave like a perfect non-covalent component, it would be reasonable to believe that the capability of melamine in interacting via its polar groups or donating and accepting hydrogen bonding has an outstanding impact on the properties of melamine-based thermosetting polymers. Several N–H, CH₂OH groups as H-donors as well as various –O–, –N= sites as H-acceptors are available on the partially butylated melamine structure to form multiple hydrogen bonding between melamine itself or with acrylic chains. Therefore, this particular chemical structure can account for the high healing of these clearcoats.

General view of the healed scratches implies that while the main trace of scratch for all clearcoats has been relatively healed, some local parts of the scratch which have been ripped in scratching are still visible and it seems that they have not been healed. Fig. 5 clearly exhibits that while the scratch trace for the pristine clearcoat (sample POSS0) is still identifiable, it has been completely disappeared for nanocoatings, indicating the higher ability of nano-structured coatings compared to that of the pure clearcoat. In order to quantify the healing ability of the coatings, profilometry technique was utilized. The profile of the bottom of the scratch before and after healing was measured. These profiles are presented in Fig. 6. The profile is given as y (altitude) against x (scratch length). The values on the vertical axis, y values, are assigned by the cone-scan software. Their absolute values are not important and therefore relative variations compared with their original surface (dashed line) have to be considered. On each profile, the minimum y (as depth), maximum y (as height, if any) and the mean y (the average of y compared to the original surface) in micron are given.

The profile of the scratches after healing for unmodified clearcoat (POSS₀) reveals that the depth of the scratch has significantly lowered. In case of all nano-structured clearcoats, it is seen that in most part of the profile, the scratched surface has returned to its original state (dashed line), but there are some local positions that the surface profile is significantly deviated from original surface. These

![Fig. 5. Optical images of scratched surfaces of various coatings loaded with different contents of POSS structure after healing process.](image-url)
Fig. 6. The profile of the bottom of the scratches for different clearcoats before and after healing.
local areas are the torn areas which have not been healed and have remained on the coating surface as a deep hole or a high hill.

The best criterion to quantify the healing could be the variations in average of $y$ which has been presented as mean $y$ and in terms of percent of variation. In other words, the percent of recovery of mean $y$ before and after healing has been calculated as presented in Table 3.

The healing ability of different coatings in Table 3 clearly shows that all clearcoats modified with POSS nano-structures have a higher ability to heal the scratches. The healing increases up to POSS10 sample after which the healing decreases. The higher healing ability of POSS-containing clearcoats will be discussed later (see DMTA section).

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $y$ (bef.) ($\mu$m)</th>
<th>Mean $y$ (aft.) ($\mu$m)</th>
<th>Healing according to mean $y$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS0</td>
<td>7.93</td>
<td>2.03</td>
<td>74.4</td>
</tr>
<tr>
<td>POSS5</td>
<td>10.66</td>
<td>1.24</td>
<td>88.3</td>
</tr>
<tr>
<td>POSS10</td>
<td>12.58</td>
<td>0.79</td>
<td>93.7</td>
</tr>
<tr>
<td>POSS15</td>
<td>12.07</td>
<td>1.95</td>
<td>83.8</td>
</tr>
<tr>
<td>POSS25</td>
<td>7.19</td>
<td>0.62</td>
<td>91.3</td>
</tr>
</tbody>
</table>

To reach a general conclusion about the effect of POSS compounds on the tribological properties of acrylic/melamine automotive clearcoats, it can be stated that incorporating low percent of POSS into clearcoat enhances its scratch resistance and hardness. Also the scratches formed on these nano-structured clearcoats can be thermally healed more efficiently compared to the unmodified clearcoats. The only defect of POSS incorporation was the appearance of some cracks at higher loadings of POSS which were unhealable. In our recent attempts to remove this defect, it was tried to toughen the nano-structured clearcoat using novel toughening agents. These modifications are in progress.

Thermo-mechanical properties of the coatings were studied to investigate the effect of POSS on some basic characteristics of the clearcoat to clarify the reasons behind the improving effect of POSS on the tribological properties.

### 3.4. DMTA analysis of POSS-containing films

Mechanical properties of thermosetting systems are highly dependent on the characteristics of the network formed during curing [49]. To study such characteristics such as cross-linking density and $T_g$, DMTA experiments were performed to elucidate the influence of POSS loading.
on films integrity. Variations of storage moduli and Tanδ versus temperature are shown in Figs. 7 and 8.

The loss factor (Tanδ) curves (Fig. 8) for neat and all modified clearcoats are similar, showing a single peak. This corresponds to compatibility between POSS and acrylic melamine matrix which forms a uniform single phase.

The values of different data deduced from DMTA graphs such as storage modulus in the rubbery plateau zone ($E'_{\text{rub}}$ used for calculation of cross-linking density), cross-linking density, $T_g$ and Tanδ width (as homogeneity factor) are given in Table 4.

As can be seen in Fig. 7 and Table 4, POSS increases the total cross-linking of the clearcoat when it is introduced to formulations. While at lower contents (POSS5 and POSS10) cross-linking density slightly increases, at higher contents of POSS (POSS15 and POSS25) it significantly increases. $T_g$ variations of the samples also reveal that as the POSS content increases $T_g$ decreases. For higher contents of POSS, however, it behaves inversely and causes a higher $T_g$ values compared to the pure clearcoat. As seen, $T_g$ does not follow a systematic trend for whole range of POSS content and is dependent on the loading percent of POSS.

In order to find out the reason for the variations in cross-linking density and $T_g$ of the modified clearcoats, it is required to investigate the effect of POSS content on the curing performance of the clearcoat. Such comprehensive investigations utilizing thermo-mechanical, thermorheological and FTIR techniques are in progress. Our rheology results (not shown here) revealed that incorporation of POSS into clearcoat causes a drop in viscosity of clearcoat. It was found that incorporation of POSS into clearcoat causes a drop in viscosity of clearcoat. It was attributed to the compact structure and lower molecular mass of POSS in comparison with linear acrylic chains which results in less extensive chain entanglements, leading to easier motion and lower viscosity. The reduced viscosity facilitates the chain motion and reaction of functional groups, leading to a more efficient curing reaction and thus higher cross-linking density.

It is observed from Table 4 that for POSS5 and POSS10 samples cross-linking density has not increased considerably compared to that of blank clearcoat. Meanwhile, for these clearcoats long linear acrylic chains have been partially replaced by a much shorter and more compact structure of POSS molecules. This replacement causes fewer and less extensive entanglements in the blend, producing a more flexible structure and thus lower $T_g$. But it seems that this behavior is not further valid at higher loadings of POSS. Considerable increase in $T_g$ of POSS15 and POSS25 clearcoats may be assigned to the their greater cross-linking density.

Tanδ width is considered as a factor relating to the homogeneity of the network formed. The lower values imply a more homogenous network. It is seen that for clearcoats containing low loading of POSS that the homogeneity increases (probably due to fewer entanglements and more compact structure of POSS) while for clearcoats loaded with high portions of POSS homogeneity decreases (due to their highly cross-linked network).

The above discussion reveals that tribological and healing data can be correlated to the basic characteristics of clearcoats (cross-linking density and $T_g$). The high scratch resistance and hardness of nano-structured clearcoats can be attributed to their high cross-linking density. In addition, shifting of SCF values for POSS-modified clearcoats (especially for those loaded with high contents of POSS) can be ascribed to the high $T_g$ and highly-crosslinked network of these clearcoats which create a hard brittle network.

The healing results of POSS clearcoats can be now explained by the changes in $T_g$ and the overall structure of clearcoats in presence of POSS nanostructures. The higher healing of clearcoats containing low loading of POSS (POSS5 and POSS10) compared to neat clearcoat and those modified with high loading of POSS can be assigned to their lower $T_g$ and their more flexible structure. In addition, POSS can affect the healing efficiency via its particular structural characteristics.

Silsesquioxanes have various Si—O—Si linkages on the cage and also on the arms together with eight hydroxyl groups on its peripheral parts. On the other hand, the monomers used in preparation of acrylic resin were styrene/ methyl methacrylate/butyl methacrylate and 2-Hydroxy ethyl methacrylate (HEMA). In spite relatively non-polar nature of these monomers which are weak or medium-strength in hydrogen-bonding formation (except for HEMA), both Si—O—Si linkages and hydroxyl groups of POSS are strong groups to interact via dipole–dipole and hydrogen-bonding with each other or other components present in the clearcoat formulation such as melamine [23]. Fig. 9 compares the H-bonding interactions in blank and POSS-containing clearcoats. Fig. 9 shows H-bondings only in one plane of POSS, but in fact these interactions are in all planes of POSS (plenty of spatial 3-dimensional interactions with the surrounding matrix). These interactions can be considered as physical cross-linkings which are thermally sensitive and can be broken at higher temperatures. The presence of extensive physical cross-linkings at ambient temperatures can guarantee the miscibility of the POSS in the matrix and also contribute to enhance the mechanical characteristics (i.e. hardness and modulus) of the network. On the other hand, loss of these types of cross-linkings at elevated temperatures facilitates the segmental motion of polymeric chains and thus the greater chance of rearrangement mechanically deformed chains. Therefore, replacing an acrylic resin composed of less polar acrylic monomers with much more polar structures (POSS) would significantly increase the intra- and inter-molecular physical forces, leading to a more healable reinforced network. These changes can be evidenced by DMTA

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$E'_{\text{rub}}$ (MPa)</th>
<th>Cross-link density (mmol/cm$^3$)</th>
<th>$T_g$ (°C)</th>
<th>Tanδ width (°C)</th>
<th>$\Delta F$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POSS$_5$</td>
<td>8.003</td>
<td>0.749</td>
<td>112.5</td>
<td>44</td>
<td>1340</td>
</tr>
<tr>
<td>POSS$_5$</td>
<td>8.13</td>
<td>0.781</td>
<td>107.8</td>
<td>41</td>
<td>1500</td>
</tr>
<tr>
<td>POSS$_{10}$</td>
<td>9.26</td>
<td>0.883</td>
<td>102.2</td>
<td>34</td>
<td>1841</td>
</tr>
<tr>
<td>POSS$_{15}$</td>
<td>24.87</td>
<td>2.158</td>
<td>136.5</td>
<td>71</td>
<td>821</td>
</tr>
<tr>
<td>POSS$_{25}$</td>
<td>33.11</td>
<td>2.923</td>
<td>134</td>
<td>75</td>
<td>990</td>
</tr>
</tbody>
</table>

$\Delta F = F_a$ (at $T = 28$ °C around ambient) – $F_m$ (at $T = 100$ °C, healing temperature).
results where the storage modulus decreases as the temperature increases from ambient to higher temperatures. The extent of storage modulus loss for all clearcoats are given in Table 4 in term of $\Delta E$ (Eq. (2)).

$$\Delta E = E_{0} (T = 28 \text{ °C around ambient}) - E_{0} (T = 100 \text{ °C, healing temperature})$$

$E_{0}$: storage modulus

It is seen that the general trend of $\Delta E$ is similar to the healing ability of the coating and the highest loss in storage modulus belongs to the most healable clearcoat (POSS$_{10}$). It is therefore can be concluded that promoting the physical interaction in the clearcoat network was a successful mechanism to enhance the healing capability of POSS containing clearcoats.

Hydrogen bond formation is usually characterized based on the shifts (in case there are sharp peaks) or variation in broadness (in case there are broad peaks) of vibration frequencies corresponding to the bonds involved in H-bonding interactions. In order to characterize the hydrogen bonding in various clearcoats, FTIR peaks corresponding to $–NH$ and $–OH$ groups can be informative. FTIR spectra of all clearcoats exhibit a broad peak around 3200–3600 cm$^{-1}$ which is assigned to various $–NH$ and $–OH$ groups on the chemical structure of clearcoats (Fig. 10).

3.5. Transparency

Transparency is a crucial property for automotive clearcoats and should not be affected when any change or new modification is made in the clearcoat formulation. Therefore, the influence of POSS addition on transparency of clearcoats was both qualitatively (Fig. 11) and quantitatively (Fig. 12) investigated. Fig. 11 depicts the visual evaluation of transparency for different clearcoats. In this picture, the word “POSS” was covered by the free films of

Presence of various $–NH$ and $–OH$ species and overlapping of $–NH$ and $–OH$ groups prevent precise characterization of hydrogen bonding. In literature, due to such limitations, the general characterization is done by measuring the width of $–NH&OH$ peak. For this purpose, the width at half height of $NH&OH$ peak ($\Delta v_{1/2}$) was measured and presented in Table 5.

Contribution of different hydrogen-bonded $NH&OH$ groups in the structure broadens this peak. The values of $\Delta v_{1/2}$ for different clearcoats clearly reveal that increase in POSS content leads to a wider $NH&OH$ peak. This may confirm the higher chance of hydrogen bonding in presence of POSS nanocages, as claimed earlier.
various clearcoats having thicknesses of 50 μm. Visual evaluation clearly demonstrates that the transparency of the POSS-containing clearcoats has not been affected. Fig. 12 quantitatively proves this. The transmission diagram for various clearcoats in the visible region is given in Fig. 12. It is seen that all clearcoats exhibit high level of transmission in the visible range. It is also revealed that POSS-containing clearcoats have the same trend as the pristine clearcoat. The mean transmission in visible region for each clearcoat was calculated and also presented in Table 5. It obviously reveals that all clearcoats have relatively higher values of transmission, indicating that not only POSS nanostructures have not changed the transparency but also it has slightly improved the optical quality probably due to the good compatibility of the POSS structure which could be efficiently blended and covalently attached to the acrylic/melamine network.

### 4. Conclusions

The effect of an OH-functional POSS on the scratch resistance and healing properties of automotive clearcoats was studied. It was found that POSS nanostructures could considerably enhance the scratch resistance of automotive clearcoats. It was attributed to the increased cross-linking of the POSS-containing clearcoats, leading to the increased

<table>
<thead>
<tr>
<th>Sample</th>
<th>POSS0</th>
<th>POSS5</th>
<th>POSS10</th>
<th>POSS15</th>
<th>POSS25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δν₁/₂ (cm⁻¹)</td>
<td>213</td>
<td>213</td>
<td>221</td>
<td>224</td>
<td>233</td>
</tr>
</tbody>
</table>

**Fig. 10.** NH&OH peak of clearcoats containing various loadings of POSS.

**Fig. 11.** Visual evaluation of transparency for different clearcoats.

**Fig. 12.** The transmission diagram and mean transmission values in visible region for all clearcoat.
hardness and elastic recovery of the coatings. In addition, all nanocomposite coatings exhibited greater capability to heal the scratches during a thermally healing process. The best healing properties were achieved by clearcoats containing low loadings of POSS. It was assigned to the lower $T_g$ values of these coating. The transparency results also confirmed that the high level of scratch resistance and healing properties was obtained without any impact on the clarity of the clearcoats.

References


[7] Yari H, Moradian S, Tahmasebi N, Arfamishesh. The best healing properties were achieved by clearcoats containing low loadings of POSS. It was assigned to the lower $T_g$ levels of these coating. The transparency results also confirmed that the high level of scratch resistance and healing properties was obtained without any impact on the clarity of the clearcoats.


