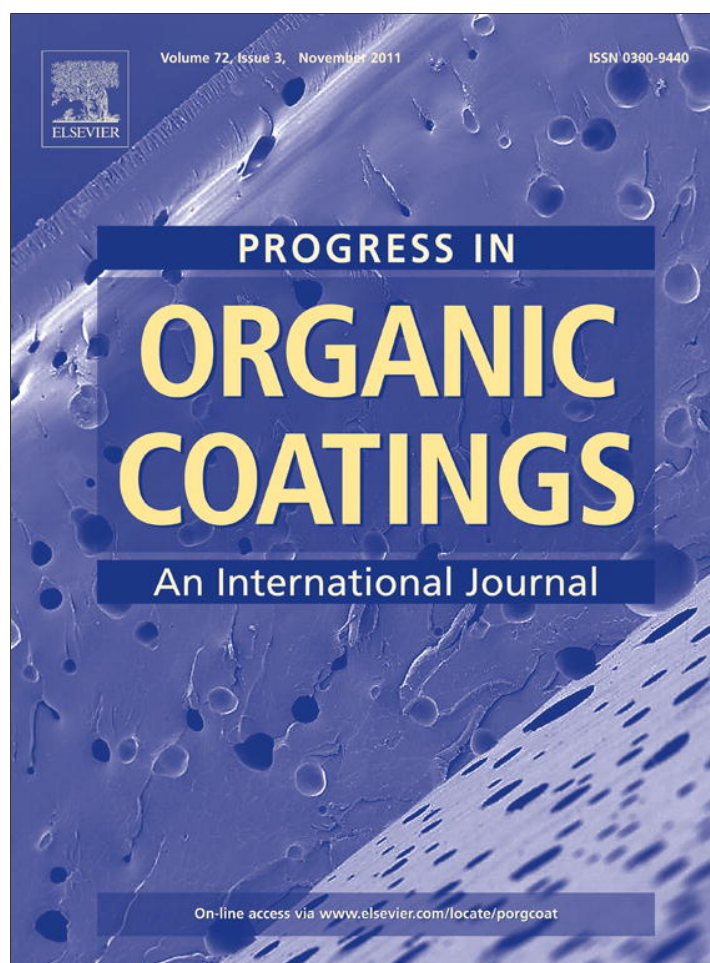


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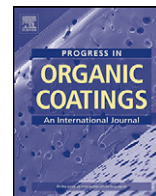
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Synthesis and characterization of novel alkyd–silicone hyperbranched nanoresins with high solid contents

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ABSTRACT

Hyperbranched alkyd–silicone nanoresins (ASiHBRs) with high solid content were synthesized by etherification reaction between a hyperbranched alkyd resin (HABR) and Z-6018 silicone. ASiHBRs were characterized by nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and several other techniques. NMR spectra show the presence of aromatic rings, –Si–O and –C–O; grafting was successful. The molar masses of ASiHBRs determined by GPC are higher than that of HABR. The hydroxyl values decrease with increasing silicone content. ASiHBRs have low viscosities what allows easier film formation. Hydrodynamic dimensions, refractive indices, glass transition temperatures, gloss and hardness of ASiHBRs increase with increasing silicone contents. Low contents of volatile organic compounds provide more environmentally friendly coatings.

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1. Introduction

Hyperbranched polymers are interesting materials due to their chemical and physical properties. They can be used in various applications such as coatings, in drug delivery, as thermosets and crosslinking agents [1]. Due to their hyperbranched structures and the presence of large numbers of functional groups in their peripheries, hyperbranched polymers exhibit lower viscosities in solution and in molten state, better solubility in common organic solvents and lower molecular entanglements degree while their molar masses are comparable to those of linear polymers [2]. Polymers in this class have high functionalities while their reactive groups are located in the peripheries – a fact that facilitates reactions with other materials [1,3].

The use of renewable resources in the preparation of various industrial materials is growing fast because of environmental concerns. In the coatings area there is the tendency towards reduction of volatile organic compounds (VOCs) – sometimes toxic and responsible for global warming and photochemical ozone creation [4]. One way to lower effects of VOCs is to use processes which provide high solid contents. It is in this context that we have

focused our attention on alkyd resins. Conventional such resins are polyesters synthesized in reactions between polyhydric alcohols such as glycerol and anhydrides such as phthalic anhydride. Fatty acids or vegetable oils are usually added to the resins to improve the flexibility and their solubility in hydrocarbon solvents [5].

Conventional alkyd resins have relatively high viscosities such as 26 Pa s [6] due to high molecular weights and linear structures resulting in large hydrodynamic volumes [2]. It is difficult to work with such resins because of the high viscosities and the resulting difficulties in formation of coatings. However, hyperbranched resins have low viscosities [6], thus easier application and coating formation.

Polymer blends and inorganic–organic hybrids can provide properties much different from their constituents [7–23]. Coatings for exterior applications require good ultraviolet (UV) radiation resistance at dry and wet conditions in a wide range of temperatures [24] while for oven applications high thermal stability is essential [25]. The alkyd resins provide good flexibility, gloss and adhesion but poor chemical resistance and low hardness [6]. On the other hand, silicon resins with their Si–O bonds and high polarity have notable thermal, oxidative and UV degradation resistance [25,26]. These properties have been incorporated in conventional alkyd resins by synthesizing alkyd–silicone copolymers [27,28]. Özgümü et al. [29] synthesized acrylic–silicone resins by free radical polymerization in solution with the objective to improve thermal and chemical stability of acrylic resins. Chojnowski et al. [30] and Tiwari et al. [31] mixed a polyimide with a polysiloxane to improve the thermal stability of the polyimide.

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Table 1
Molar ratios of Z-6018 silicone to HABR and initial percentages of Si in the synthesis.

Resins	Z-6018/HABR ratio	Si initial percentage
ASiHBR1	0.34	2.04
ASiHBR2	0.62	3.75
ASiHBR3	0.86	5.19
ASiHBR4	1.06	7.23

Coatings based on epoxy cycloaliphatic/caprolactam were mixed with caprolactam polyols functionalized with siloxane for improvement of mechanical properties [32]. Thus, coatings with antifouling and antibacterial properties have been obtained. Kanai et al. [33] modified a conventional alkyd resin based on soybean oil with silicone/acrylic copolymer for better mechanical properties. Easton and Poultney [13] modified alkyd resins with silicone for obtaining weather resistant resins. Park et al. [34] synthesized acrylic/silicone resins for weather resistant coatings. Yanagase and Ito [35] synthesized silicone/acrylic resins as impact modifiers of poly(vinyl chloride) and poly(methyl methacrylate). Tiwari et al. [36] developed a silicone coating to be used as an anticorrosive protection.

So far there has been no report in the literature of alkyd–silicone hyperbranched resins with high solid content. Such resins should be appropriate for surface coatings on metal bridges, towers, rails and ships. We expect comparable uses as those of polyurethane coatings – while the latter require certain precautions in terms of health [25].

In the present work a hyperbranched alkyd resin (HABR) was modified with hydroxyl-terminated silicone (Z-6018 silicone) through etherification reaction. Properties of the film of that resin with high solid content have been compared with those of films of silicone–alkyd hyperbranched resins (ASiHBRs) of the same solid content. Furthermore, the effect of the proportion of Z-6018 silicone used on several properties of ASiHBRs has been studied.

2. Experimental

2.1. Materials

Hydroxyl-terminated silicone (Z-6018 silicone) was obtained from Dow Corning. The silicone is not a pure compound but a mixture of phenyl, propyl silsesquioxanes (>60%) and a hydroxy-terminated linear siloxane. A hyperbranched alkyd resin (HABR) was synthesized as reported before [37]. Tetrahydrofuran, sodium hydroxide, potassium hydroxide, xylene, p-toluenesulfonic acid (PTAS), sodium chloride and hydrochloric acid, were purchased from Aldrich and used as received. Calcium, zirconium and cobalt octoate were supplied by Colorquímica and also used as received.

2.2. Synthesis of the resins

HABR was mixed with Z-6018 silicone and p-toluenesulfonic acid (0.1%). The system was heated at 120 °C and kept at constant mixing under nitrogen atmosphere. The reaction took place during 60 min. Xylene was added to the reactor for obtaining ASiHBRs with the solid content of $\approx 70\%$. Molar ratios of the silicone to HABR and the initial percentages of Si in the resins are listed in Table 1. The synthesis is shown in Fig. 1.

2.3. Characterization of the ASiHBRs

Before NMR analysis, the samples were subjected to Soxhlet extraction during 24 h using hexane as the solvent to eliminate the silicone residue and to separate the silicone polymer formed. NMR

analysis was performed using a Bruker AC 300 MHz spectrometer with chloroform as the solvent.

Hydroxyl values were determined according to ASTM D-4274 standard. The analyses were performed in duplicate.

Gel permeation chromatography (GPC) was performed in Waters 600 equipment using a styragel column with dimensions of 4.6×300 mm. The samples were dissolved in tetrahydrofuran and the runs performed at 30 °C. Millennium 2000 software was used for data acquisition with linear polystyrene as the standard.

Rheological analysis was performed using a cylindrical geometry at 2% strain with a MRC 301 rotational rheometer of Anton Paar. Dynamic light scattering analysis (DLS) of the solutions was conducted on a zetasizer Nano S series machine from Malvern Instruments at the 633 nm wavelength. Differential scanning calorimetry (DSC) was performed in a TA Instrument model Q100 equipped with a refrigerated cooling system, at the heating and cooling rate of 30 °C/min under nitrogen atmosphere.

The refractive indices were determined using an Abbe refractometer at the 589 nm wavelength.

The iodine values were determined according to the ASTM D 1959 standard.

In order to analyze film properties, the resins were mixed with solutions of cobalt octoate (0–4 wt.), calcium octoate (0–4 wt.) and zirconium octoate (0–4 wt.), by using a film applicator. The films were applied on steel surfaces and dried at 25 °C under relative humidity of 40%.

Adhesion was measured using a cross-hatch cutter; the test is based on ASTM D 3359. The flexibility of ASiHBRs was determined according to ASTM D 522. We have used Braive Instruments conical mandrel bending 1510 tester. Specular gloss measurements based on ASTM D 523 were performed on leneta substrates at 60° and 85° using an Elcometer. The drying time of the resins was taken as the time required to obtain a tack-free film, the test based on ASTM D 1640. Chemical resistance of the HABRs was determined using water, sodium chloride (NaCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH). The samples were placed in the solvent for 6 h at room temperature. The thickness of wet films was 52 μm in all cases.

3. Results and discussion

3.1. NMR results (^{13}C)

ASiHBR1 was chosen due to its low proportion of the Z-6018 silicone employed in the synthesis. Fig. 2a presents the overall spectrum and Fig. 2b a magnified aromatic carbon region. The signal around 167 ppm corresponds to C=O groups; at 130 ppm appears a signal due to C=C bonds (Fig. 2a). The signals at 125 ppm are due to aliphatic carbons bonded to Si and to aromatic carbons.

The signal at 70 ppm corresponds to chloroform while at 60 ppm appear signals due to CH_2 bonded to Si–O (–Si–OCH₂) and C–O (Fig. 2a). Around 50 ppm there are signals corresponding to quaternary carbons of the terminal, linear and dendritic units; the signals between 0 and 40 ppm are assigned to CH_3 (around 15 ppm), $\text{CH}_3\text{–CH}_2\text{–}$ (23 ppm), $\text{CH}_2\text{COO–}$ (26 ppm), $\text{CH}_3\text{–(CH}_2)_2$ (33 ppm) and CH_2COOR (35 ppm). The presence of the resins signals corresponding to aromatic rings, ether groups and Si–O provide evidence of formation of the ASiHBR1.

3.2. Numbers of hydroxyl groups and related parameters

ASiHBRs may contain residual silanol groups – what affects the determination of OH groups of the HABR resins; due to OH groups of the ASiHBRs, unreacted (C–OH) and residual silanol groups (Si–OH)

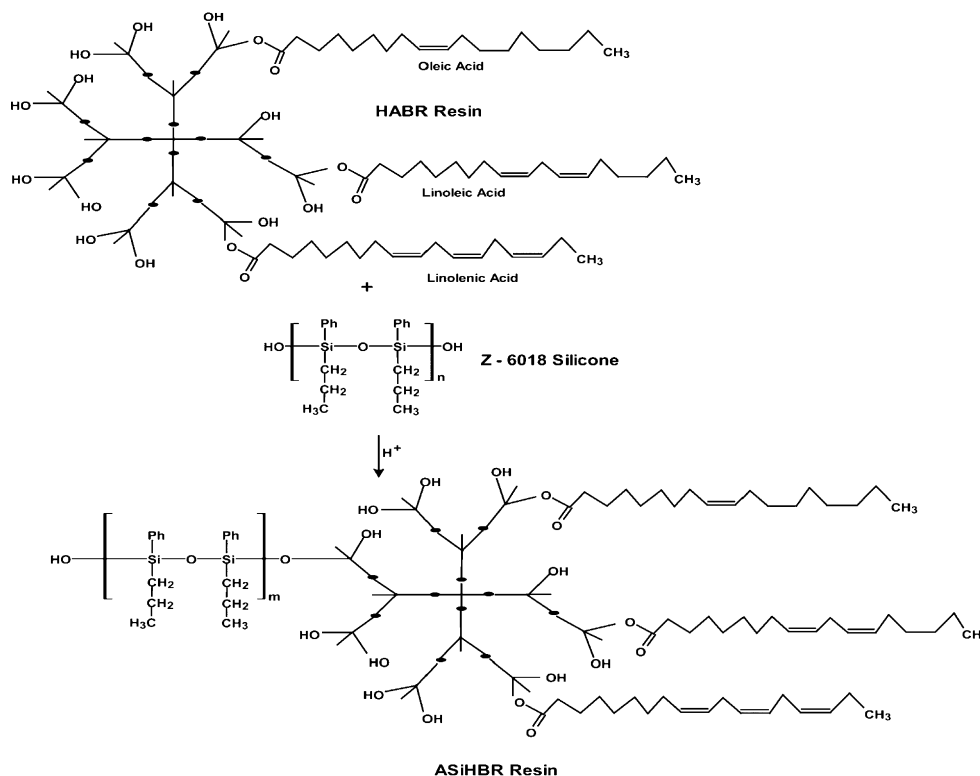


Fig. 1. Structural representation of synthesis of ASiHBR resins.

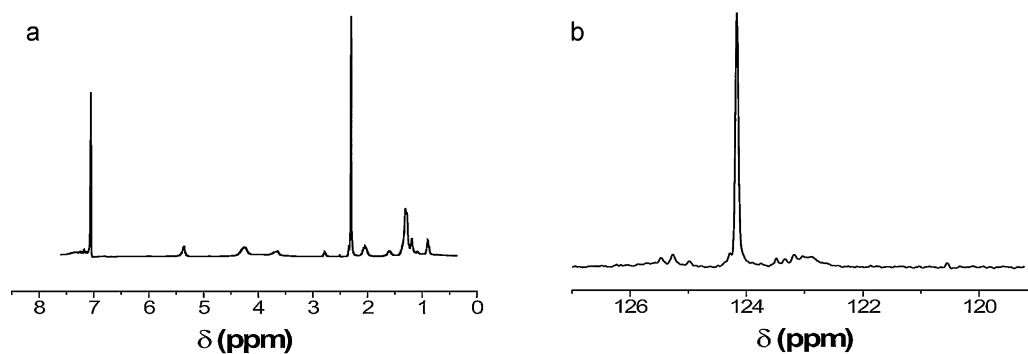


Fig. 2. (a) ¹³C NMR spectrum of the ASiHBR1 resin; (b) magnified aromatic region.

may be acetylated. Percentage changes in the hydroxyl values V_{OH} caused by the reaction for ASiHBR 1–4 samples were calculated as:

$$\Delta V_{OH} = \left[\frac{A - B}{A} \right] \times 100\% \quad (1)$$

Here A and B are V_{OH} values respectively of one of the ASiHBRs (1–4446 mg KOH/g sample) and the HABR. The number N_{OH} of modified OH groups per molecule of any ASiHBR is

$$N_{OH} = \frac{\Delta V_{OH} - N_{TOH}}{100} \quad (2)$$

Here N_{TOH} is the number of terminal OH groups of the ASiHBR sample in the periphery of the molecule calculated from NMR results [35]. The number N_{nOH} of OH groups per molecule of ASiHBR that did not undergo modification is

$$N_{nOH} = N_{TOH} - N_{OH} \quad (3)$$

Table 2 lists values of parameters calculated from the above equations. The hydroxyl value V_{OH} and the average number of OH

Table 2

Number of hydroxyl groups and related parameters for ASiHBR resins.

Resins	V_{OH}	ΔV_{OH}	N_{OH}	N_{nOH}
ASiHBR1	168.38	26.96	2.51	6.79
ASiHBR2	145.30	36.97	3.44	5.86
ASiHBR3	112.33	51.39	4.79	4.51
ASiHBR4	72.24	68.66	6.38	2.92

groups on the periphery per macromolecule of the HABR resin were respectively 230.5 mg KOH/g sample and 9.30.

V_{OH} values of the ASiHBR resins decrease with increasing amounts of the Z-6018 silicone used. This result was expected since enhancing the proportion of the silicone makes higher the probability of modification of OH groups on the periphery of the HABR resin. This tendency is seen in grafting the silicone on the HABR resin.

3.3. Gel permeation chromatography results

Table 3 provides values of the number average molar mass M_n , the weight average molar mass M_w and the polydispersity index

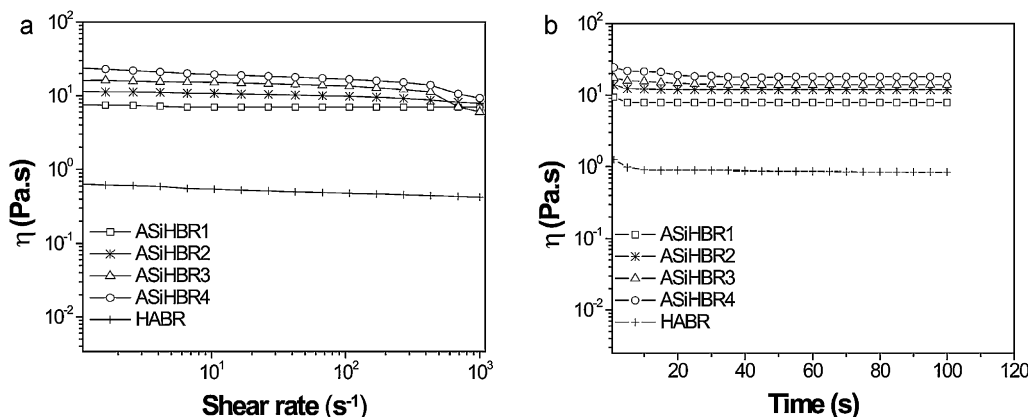


Fig. 3. (a) Viscosity η vs. shear rate of the resins; (b) viscosity η vs. time of the resins.

Table 3

M_n , M_w and PI values for the ASiHBR resins.

ASiHBR resins	M_n (g/mol)	M_w (g/mol)	PI
ASiHBR1	5.34×10^3	1.75×10^4	3.28
ASiHBR2	5.89×10^3	2.00×10^4	3.40
ASiHBR3	7.28×10^3	2.69×10^4	3.69
ASiHBR4	9.14×10^3	3.53×10^4	3.87

$PI = M_w/M_n$ of our resins. M_n values of the ASiHBRs are higher than M_n for the HABR resin = 4.46×10^3 g/mol [37] – an indication that the reaction between the HABR and the silicone did occur in all cases.

M_n , M_w and PI values go symbatically with the amount of the silicone – as now expected. The increase of PI shows that higher concentrations of the silicone result in larger variations of the numbers of silicone units grafted.

3.4. Rheological behavior

Viscosity η vs. shear rate diagrams of the resins are displayed in Fig. 3a. We see that η of the ASiHBRs increases with M_n values and is higher than the value for the HABR of the same solid content. The last result can be explained by higher M_n values and by the presence of voluminous phenyl groups. The η values of the resins in Pa s at the shear rate of 1.12 s^{-1} are: 7.42 for ASiHBR1; 11.3 for ASiHBR2; 16.1 for ASiHBR3; 23.3 for ASiHBR4, 23.3; and 0.625 for HABR.

In the range of shear rates studied, all resins display a small reduction of viscosity with increasing shear. ASiHBR3 and ASiHBR4 show a larger reduction of viscosity at the shear rate of 700 s^{-1} . This can be explained by the presence of entanglements of the chains or the presence of linear unreacted silicone polymer of the silicone. Linear polymers with entanglements undergo a viscosity decrease when unentanglements occur [38]. We recall that in Brownian dynamics simulation of flow of polymer solutions, the flow causes lowering of the number of entanglements per unit volume [39,40]. Another explanation of the reduction on viscosity of the ASiHBR3 and ASiHBR4 resins is due to rupture of the phenyl group interactions; this according to a hypothesis by Bat et al. [4]. ASiHBR3 and ASiHBR4 have relatively high numbers of silicone units in their structures and therefore high numbers of phenyl groups.

Viscosities of our resins are lower than those of conventional (linear) alkyd resins that do not have high solid content obtained by Patel et al. (values between 148 and 186 Pa s) [41] or those by Manczyk and Szweczyk (20–1000 Pa s) [6].

Table 4

Average diameters for the ASiHBRs.

ASiHBR Resins	d_1 (nm)	d_2 (nm)	d_3 (nm)
ASiHBR1	21 (7.0%)	352 (93.0%)	–
ASiHBR2	34 (5.6%)	378 (92.7%)	5560 (1.7%)
ASiHBR3	20 (24.2%)	433 (71.0%)	5052 (4.8%)
ASiHBR4	45 (5.9%)	614 (89.0%)	5421 (5.1%)

Fig. 3b shows diagrams of viscosity η vs. time t at the 200 s^{-1} shear rate. We see that the viscosities hardly change with the time, all resins have high time stability.

3.5. Dynamic light scattering

Diagrams for ASiHBR1 and ASiHBR2 are shown in Fig. 4. These resins are polydisperse due to differences in grafting of the silicone onto the HABR. The polydispersity is lower for ASiHBR1 – only two peaks – than for ASiHBR2. We recall that less silicone was employed in the synthesis of ASiHBR1.

Table 4 lists values of hydrodynamic dimensions of our ASiHBRs. From left to right, d_1 is the first diameter, d_2 is the second and d_3 is the third. The first diameter d_1 apparently reflects macromolecules formed in hydroxy–ester interchange reaction. That reaction is shown in Fig. 5.

The second diameter (d_2) reflects formation of ASiHBRs resins and is in accordance with M_n values.

All ASiHBRs show higher values of hydrodynamic diameters than the HABR (93 nm) [37]. Again we have agreement with results reported in Section 3.5.

The third diameter d_3 values correspond to the presence of linear polymers (residues of the silicone or the silicone polymer) which have high hydrodynamic volumes compared to hyperbranched polymers. Variations in hydrodynamic diameters of our ASiHBRs resins reflect the fact that the grafting was not complete (competition among silicone molecules for grafting sites on HABR).

3.6. Differential scanning calorimetry results

Fig. 6 shows the DSC thermograms of our ASiHBRs. Glass transition temperatures T_g have been evaluated from changes in slope. T_g values increase with increasing silicone contents: $T_g = -6^\circ \text{C}$ for ASiHBR1, -2°C for ASiHBR2, $+4^\circ \text{C}$ for ASiHBR3 and $+9^\circ \text{C}$ for ASiHBR4. We note that the T_g values obtained are related to the technique used [42]. The present results can be explained by increasing M_n values along with increased silicone concentration. In nonlinear

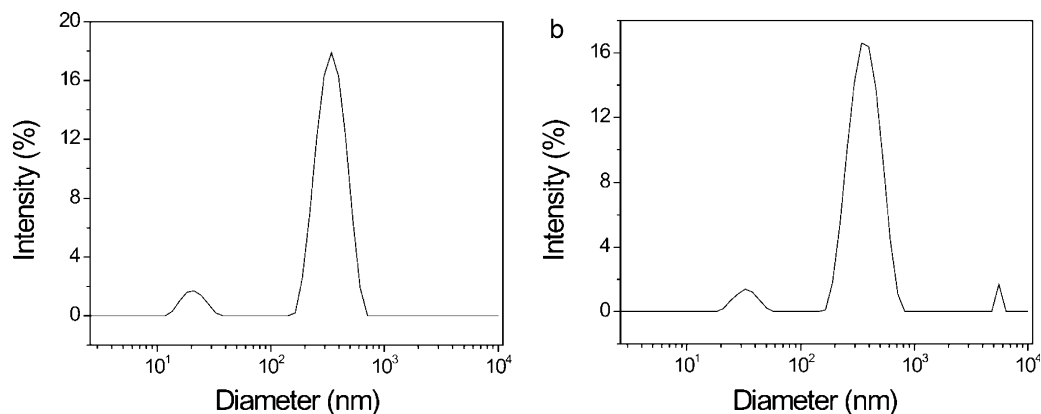


Fig. 4. Intensity size distributions: (a) ASiHBR1; (b) ASiHBR2.

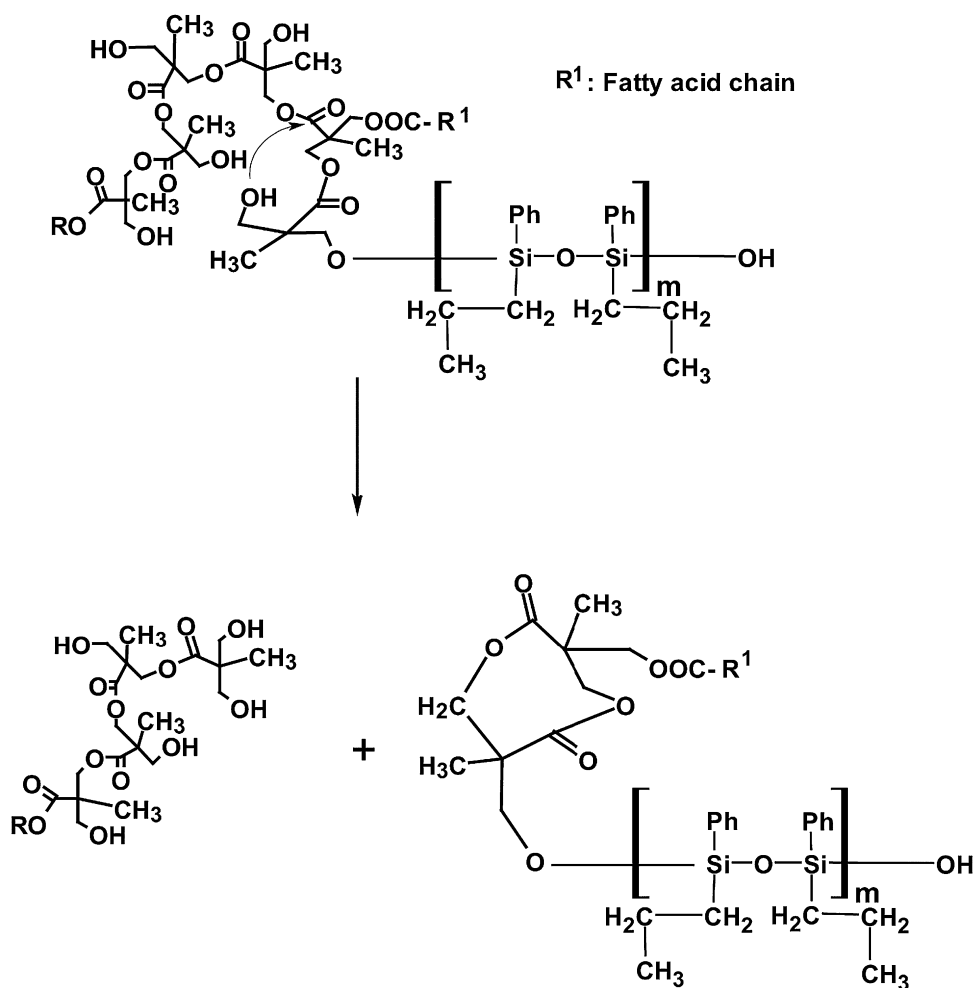


Fig. 5. Schematic representation of the hydroxy – ester interchange reaction.

polymers this in turn decreases the mobility of the macromolecules and causes a T_g increase.

3.7. Iodine values (VI_2), refractive indices and color

The iodine value and refractive index results are presented in Table 5. The iodine values represent a measure of unsaturation and are expressed in terms of the number of centigrams of iodine absorbed per gram of sample. These values decrease with the silicone contents increase since the concentration of double bonds per

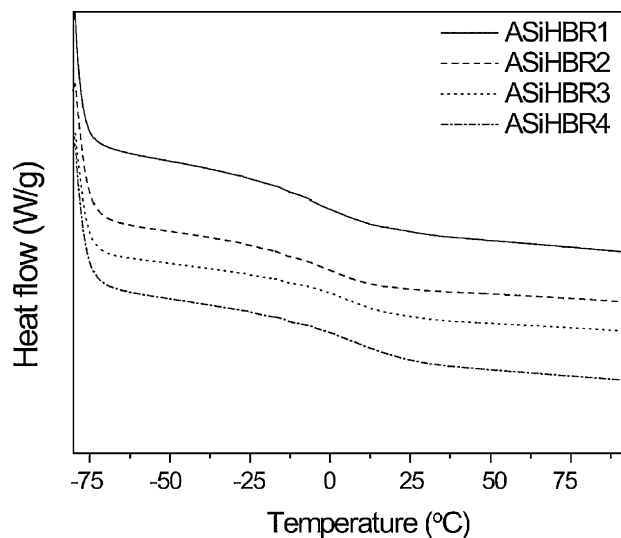
Table 5
Iodine values, refractive indices and color of ASiHBR resins.

HBP	Iodine value (g I ₂ /100 g of sample)	Refractive index	Color
ASiHBR1	54.17	1.4944	Light yellow
ASiHBR2	50.74	1.4973	Light yellow
ASiHBR3	45.96	1.4992	Light yellow
ASiHBR4	38.33	1.5023	Light yellow

Table 6

Gloss, adhesion, flexibility and drying time of the resins.

Resins	Gloss (leneta) 60°/85°	Adhesion (%)	Flexibility	Drying time (min)	Hardness (h_{Vickers})
ASiHBR1	91.1/99.7	92	Pass	240	6.94
ASiHBR2	91.5/100.2	100	Pass	216	8.64
ASiHBR3	91.8/100.5	100	Pass	194	9.87
ASiHBR4	92.0/100.8	100	Pass	177	12.02
HABR	85.2/91.7	85	Pass	260	4.00

**Fig. 6.** DSC thermograms of the ASiHBRs.

gram of the resin decreases. In all cases the iodine values for our ASiHBRs are lower than for HABR [37].

The refractive index changes are related to the increase of molecular weight and electronic density of the ASiHBRs. The color of the ASiHBR resins is light yellow but darker than that of the HABR.

3.8. Film properties

We have determined gloss, adhesion, flexibility, drying time and hardness; the results are presented in Table 6. Films properties of the ASiHBRs are compared with the HABR of the same solid content.

3.8.1. Gloss

The gloss of ASiHBRs is higher than that of HABR. Wicks et al. [43] have reported that silicones have excellent gloss. The gloss values of the ASiHBRs increase slightly with the content of the silicone employed on the synthesis.

3.8.2. Adhesion

The adhesion is higher for the ASiHBRs than for HABR. Apparently higher adhesion – that is stronger interfacial interactions – increase with increasing number of R–Si–OR groups [44].

3.8.3. Flexibility and drying time

The flexibility of ASiHBRs is satisfactory. ASiHBRs have shorter drying times than HABR. The drying time corresponding to tack-free film formation, is favored by increases of T_g and molar mass [43] and in our materials also by an increase in silicone concentration.

3.8.4. Vickers hardness

We now consider h_{Vickers} results. The hardness enhances with the silicone content; in fact silicone materials have been employed to achieve higher hardness [29]. In all cases the hardness of ASiHBRs

Table 7

Chemical resistance of the resins.

Resins	Water	HCl (0.1 M)	NaOH (0.1 M)	NaCl (5%)
ASiHBR1	A	A	A	A
ASiHBR2	A	A	A	A
ASiHBR3	A	A	A	A
ASiHBR4	A	A	A	A
HABR	A	A	C, D	A

(A) Without removal; (B) totally removed; (C) partially removed; and (D) blister.

is much higher than that of HABR. We recall DSC results reported above: free volume in ASiHBRs is smaller, therefore the cooperative movement of the macromolecular chains is constrained more.

We also recall that during scratch resistance determination for polymers one observes formation of two top ridges along the groove formed by the passage of the indenter [45,46]. It has been demonstrated that the joint cross-sectional surface area of the groove and the two top ridges is a function of Vickers hardness [47]. Namely, the higher h_{Vickers} , the lower is the cross-sectional area; an equation in which h_{Vickers} is in an exponential term describes that relationship.

3.9. Chemical resistance

Table 7 presents results of determination of chemical resistance of the resins. The chemical resistance of our ASiHBRs is quite satisfactory. Ether groups in our ASiHBRs resins are more resistant to hydrolytic degradation than ester groups [48].

4. A survey of results

We have synthesized new environmentally friendly resins which can be employed in the coatings industry. The rheological behavior of the HBRA resins was mainly Newtonian and our materials show high stability in time. In all cases the reaction between HABR and 6018-silicone took place – as evidenced by analytical techniques employed in this study. All ASiHBR resins contain unreacted hydroxyl groups; therefore, these materials can be modified by other materials such as maleic anhydride or amines for obtaining waterborne resins. Film properties of the ASiHBR resins are better than those of the HABR, including higher adhesion (stronger interfacial interactions), shorter drying times, higher hardness and higher gloss.

References

- [1] D.A. Tomalia, Prog. Polym. Sci. 30 (2005) 294.
- [2] W. Brostow, H.E. Hagg Lobland, S. Pal, R.P. Singh, J. Mater. Ed. 31 (2009) 157.
- [3] E.A. Murillo, P.P. Vallejo, L. Sierra, B.L. López, J. Appl. Polym. Sci. 112 (2009) 200.
- [4] E. Bat, G. Gunduz, D. Kisakurek, I.M. Akhmedov, Prog. Org. Coat. 55 (2006) 330.
- [5] O. Saravari, P. Phapant, V. Pimpan, J. Appl. Polym. Sci. 96 (2005) 1170.
- [6] K. Manczyk, P. Szewczyk, Prog. Org. Coat. 44 (2002) 99.
- [7] X. Kong, E. Ruckenstein, J. Appl. Polym. Sci. 73 (1999) 2235.
- [8] M. Barrere, F. Ganachaud, D. Bendejacq, M.A. Dourges, C. Maitre, P. Hemery, Polymer 42 (2001) 7239.
- [9] I. Marcu, E. Daniels, V. Dimonie, C. Hagiopol, J. Roberts, M. El-Aasser, Macromolecules 36 (2003) 328.
- [10] V. Castelvetro, C. De Vita, Adv. Colloid Interface Sci. 108 (2004) 167.
- [11] E.A. Murillo, B.L. López, Macromol. Symp. 242 (2006) 131.

- [12] B. Bilyeu, W. Brostow, L. Chudej, M. Estevez, H.E. Hagg, J.R. Rodriguez, S. Vargas, *Mater. Res. Innovat.* 11 (2007) 181.
- [13] T. Easton, S. Poultney, *J. Coat. Technol. Res.* 4 (2007) 187.
- [14] W. Brostow, T. Datashvili, *Mater. Res. Innovat.* 11 (2007) 127.
- [15] W. Brostow, T. Datashvili, K.P. Hackenberg, *e-Polymers* 054 (2008) 1.
- [16] L.F. Giraldo, W. Brostow, E. Devaux, B.L. Lopez, L.D. Perez, *J. Nanosci. Nanotechnol.* 8 (2008) 3176.
- [17] W. Brostow, W. Chonkaew, K.P. Menard, T.W. Scharf, *Mater. Sci. Eng. A* 507 (2009) 241.
- [18] V.H. Orozco, W. Brostow, W. Chonkaew, B.L. Lopez, *Macromol. Symp.* 277 (2009) 69.
- [19] L.F. Giraldo, B.L. Lopez, W. Brostow, *Polym. Eng. Sci.* 49 (2009) 896.
- [20] A.F. Vargas, W. Brostow, H.E. Hagg Lobland, B.L. Lopez, O. Olea-Mejia, *J. Nanosci. Nanotechnol.* 9 (2009) 6661.
- [21] M.D. Bermudez, W. Brostow, F.J. Carrion-Vilches, J. Sanes, *J. Nanosci. Nanotechnol.* 10 (2010) 6683.
- [22] O. Olea-Mejia, W. Brostow, E. Buchman, *J. Nanosci. Nanotechnol.* 10 (2010) 8524.
- [23] P. Blaszcak, W. Brostow, T. Datashvili, H.E. Hagg Lobland, *Polym. Compos.* 31 (2010) (1909);
(b) W. Brostow, M. Dutta, P. Rusek, *Eur. Polym. J.* 46 (2010) 2181.
- [24] F.N. Jones, *Alkyd Resins in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2005, p. 1.
- [25] R. Wollast, A. Toussaint, *J. Paint Technol.* 34 (1967) 34.
- [26] M.D. Soucek, D.P. Dworak, R. Chakraborty, *J. Coat. Technol. Res.* 4 (2007) 263.
- [27] V.R. More, N.G. Malvankar, D. Kumar, *RMNL Rep. on Syn. of Silicone-Soya Alkyd*, 1996.
- [28] J. Alam, U. Riaz, S. Ahmad, *Curr. Appl. Phys.* 9 (2009) 80.
- [29] S. Özgümü, T.B. Yim, I. Acar, E. Küçükolu, *Polym. Adv. Technol.* 18 (2007) 213.
- [30] J. Chojnowski, M. Cypriak, W. Fortuniak, M. Scibiorek, K. Rozga-Wijas, *Macromolecules* 36 (2003) 3890.
- [31] A. Tiwari, A.K. Nema, C.K. Das, S.K. Nema, *Thermochim. Acta* 417 (2004) 133.
- [32] S. Wu, M.T. Sears, M.D. Soucek, *Prog. Org. Coat.* 36 (1999) 89.
- [33] T. Kanai, T.K. Mahato, D. Kumar, *Prog. Org. Coat.* 58 (2007) 259.
- [34] H.S. Park, I.M. Yang, J.P. Wu, M.S. Kim, H.S. Hahm, S.K. Kim, H.W. Rhee, *J. Appl. Polym. Sci.* 81 (2001) 1614.
- [35] A. Yanagase, M. Ito, *J. Polym. Sci. Part A: Polym. Chem.* 42 (2004) 1112.
- [36] A. Tiwari, J. Zhu, L.H. Hihara, *Surf. Coat. Technol.* 202 (2008) 4620.
- [37] E.A. Murillo, P.P. Vallejo, Betty L. Lopez, *Prog. Org. Coat.* 69 (2010) 235.
- [38] S. Uppulury, S.E. Keinath, D.A. Tomalia, P.R. Dvornic, *Macromolecules* 31 (1998) 4498.
- [39] W. Brostow, M. Drewniak, N.N. Medvedev, *Macromol. Theory Simul.* 4 (1995) 745.
- [40] W. Brostow, M. Drewniak, *J. Chem. Phys.* 105 (1996) 7135.
- [41] V.C. Patel, J. Varughese, P.A. Krishnamoorthy, R.C. Jain, A.K. Singh, M. Ramamoorthy, *J. Appl. Polym. Sci.* 107 (2008) 1724.
- [42] W. Brostow, S. Deshpande, D. Pietkiewicz, S.R. Wisner, *e-Polymers* 109 (2009) 1.
- [43] Z.W. Wicks, F.N. Jones, S.P. Pappas, *Org. Coat. Sci. & Tech.*, vol. I, John Wiley & Sons, New York, 1994, p. 259.
- [44] M. Esfandeh, S.M. Mirabedini, S. Pazokifard, M. Tari, *Colloids Surf. A: Phys. Eng. A* 302 (2007) 11.
- [45] W. Brostow, J.-L. Deborde, M. Jaklewicz, P. Olszynski, *J. Mater. Ed.* 25 (2003) 119;
W. Brostow, V. Kovacevic, D. Vrsaljko, J. Whitworth, *J. Mater. Ed.* 32 (2010) 273.
- [46] W. Brostow, H.E. Hagg Lobland, M. Narkis, *J. Mater. Res.* 21 (2006) 2422.
- [47] W. Brostow, W. Chonkaew, L. Rapoport, Y. Soifer, A. Verdyan, *J. Mater. Res.* 22 (2007) 2483.
- [48] L. Chikh, M. Tessier, A. Fradet, *Polymer* 48 (2007) 1884.