

Consolidation and ageing features of vinylneodecanoate-containing in adhesive films used as a support for museum textiles

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In order to improve the ageing resistance of adhesive films used as a support for museum textiles, the units of vinyl acetate in an adhesive copolymer were replaced by the units of vinyl neodecanoate 10 (Veova). Several Veova terpolymers and tetrapolymers with various (meth)acrylates were synthesized and studied. The composition of the new copolymers was calculated referring to both acid value and integral signals in ¹H-NMR spectra. The coating features of the new adhesives on a supporting silk fabric were evaluated. It was determined that the tetrapolymers containing about 15 mol.% of Veova units, 5 mol.% of AA units and the right ratio of the units of MMA and BA met the requirements for textile adhesives. Changes in the chemical structure of the copolymers under artificial ageing were assessed by ATR-FTIR spectroscopy, including difference spectra obtained by subtracting the spectrum of a control sample from the spectrum of the artificially aged samples. The spectral data revealed auto-oxidative processes taking place under ageing, leading to rupture of the lateral Veova groups in the initial stage of the process and a cleavage of the polymer main chain under a prolonged artificial ageing of the adhesive layers.

Key words: vinyl neodecanoate, Veova, adhesive film, ageing stability, difference FTIR spectra

INTRODUCTION

Environmental conditions, namely light, fluctuations of relative humidity and temperature, atmospheric pollution, and human negligence usually cause deterioration of textile artefacts. After dismantling and cleaning procedures of a deteriorated textile artefact, textile conservators have to choose an optimal method to support it in order to keep its shape and strengthen its thread. For this purpose, a supporting silk fabric is used [1–5], which is stitched down or adhered to the original textile artefact.

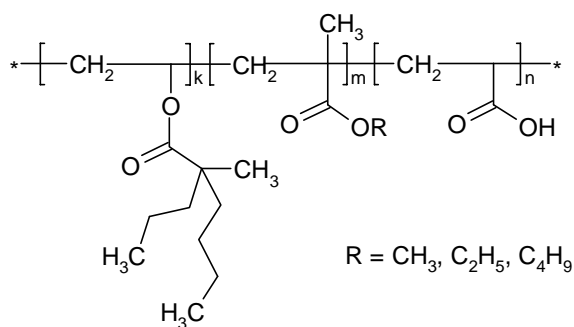
After numerous tests, specialists of P. Gudynas Restoration Centre (a branch of the Lithuanian Art Museum) introduced into the area of conservation a support technique using the poly(vinyl acetate-acrylate) resin based adhesive called A-45K (*Polymer*, Russia). This technique has been under development since 1982 [6], and the use of this adhesive to support textile collections has been adopted by conservation workshops throughout Lithuania and the neighbouring countries. Recently, the changes in the chemical structure of the poly(vinyl acetate-acrylate) based adhesive have been evaluated using the difference ATR-FTIR spectra obtained by subtracting the spectrum of a control sample from the spectrum of na-

turally or artificially aged one [7, 8]. Simultaneous decrease in the relative absorbance of negative-going features of the modes, which are characteristic of vinyl acetate, provide an unambiguous evidence of degradation of these polymeric segments of the adhesive under natural or artificial ageing in light. The acetate group of the poly(vinyl acetate-acrylate) copolymer takes part in the degradation and derivatization reactions that are relatively faster than with the acrylate group. These results correlate well with the opinion that the photo-stability of aliphatic (meth)acrylic polymers is usually high, for instance, much higher than that of polyolefins [9–12].

In order to improve the ageing resistance of the adhesive layers used in the lining of museum textiles, we attempted to replace the units of vinyl acetate in the copolymer studied before [7] with the units of vinyl neodecanoate 10 (Veova). It is known [13] that Veova units impart a combination of flexibility, hydrophobicity and very good chemical and UV resistance. Moreover, these units add steric bulk to the polymer, providing protection to the less stable monomers like vinyl acetate. The structural formula of the copolymer studied in the present work is presented in Scheme 1.

The aim of this work was to find the optimal composition of vinyl neodecanoate-acrylate-based copolymers and to study the coating features of novel copolymers

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Scheme 1. Structural formula of vinyl neodecanoate 10 – acrylate copolymer

on the supporting silk fabric. The films of these copolymers have been exposed to the artificial light (ultraviolet (UV) irradiation), and the structural changes during the ageing process have been followed using an attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR). The changes were verified by measuring auxiliary features of the films, such as optical properties, acidity and solubility.

EXPERIMENTAL

Materials

The monomers methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA) and vinyl acetate (VAC), all *Fluka* products, were purified following an ordinary distillation procedure under reduced pressure.

The monomer vinyl neodecanoate 10 (vinyl ester of neodecanoic (versatic) acid, VeoVa) was purchased from *Resolution Performance Products (UK)* and used without purification.

The monomers ethyl methacrylate (EMA) and butyl methacrylate (BMA), both purchased from *Aldrich*, were used without purification.

The initiator α,α' -azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol.

Synthesis procedures

Three- or tetra-component copolymers were synthesized by free radical polymerization in ethyl acetate solution at 70 °C using AIBN as an initiator. The total concentration of the monomers VeoVa, MMA, EMA, BMA, BA and AA was ca 28 wt%, the concentration of the initiator being 0.2 wt%.

A feed of the monomers (5 g) was dissolved in ethyl acetate giving 20 ml of solution. Glass ampoules filled up with reaction mixtures were purged with nitrogen and sealed. Copolymerization was carried out for 5 h (10 h in some cases) in a water thermostat, then the ampoules were cooled and opened. The copolymer VeoVa-35 (initial feed of the monomers at the ratio VeoVa : MMA : BA : AA = 35 : 30 : 30 : 5 mol%) was precipitated by pouring the reaction mixture into petrol ether and purified by dissolving in benzene and reprecipitating to hexane. The copolymer VeoVa-25 was precipitated by pouring the reaction mixture to methanol and reprecipitated

from acetone. All copolymers were dried in the air for two days, then in a vacuum oven at 37 °C for 10 h.

Analysis procedures

The intrinsic viscosity of the copolymer solutions in benzene at 25 °C was determined using a Ubbelohde type viscometer. Intrinsic viscosity was calculated by the extrapolation of inherent viscosity and reduced viscosity to zero concentration following common procedures [14, 15].

The composition of the copolymers was calculated referring to both acid value and integral signals in ¹H-NMR spectra.

The acid value of the copolymers was determined by the titration of their benzene solutions [15]. The amount of acrylic acid units in a copolymer was calculated as follows:

$$K_{AA} = \frac{N_A}{L} \cdot 100\%$$

where K_{AA} – amount of AA units in a copolymer, wt%; N_A – acid value determined experimentally, mg KOH/ g; L – acid value of poly(acrylic acid), 778 mg KOH/ g.

The amount of VeoVa, BA and MMA units in a copolymer was calculated by comparing analytical signals of protons in $-\text{CH}_2-\text{CH}(\text{OCOR})-\text{CH}_2-$, $-\text{CO}-\text{O}-\text{CH}_2-\text{R}$ and $-\text{CO}-\text{O}-\text{CH}_3$ recorded at 4.81, 4.00 and 3.68 ppm, respectively (Fig. 1). Since the signal at 4.81 ppm was very weak in the spectra of most copolymers, the copolymer composition was calculated by comparing the integrals of the signals at 4.00 and (or) 3.68 ppm with the integral of the whole spectrum.

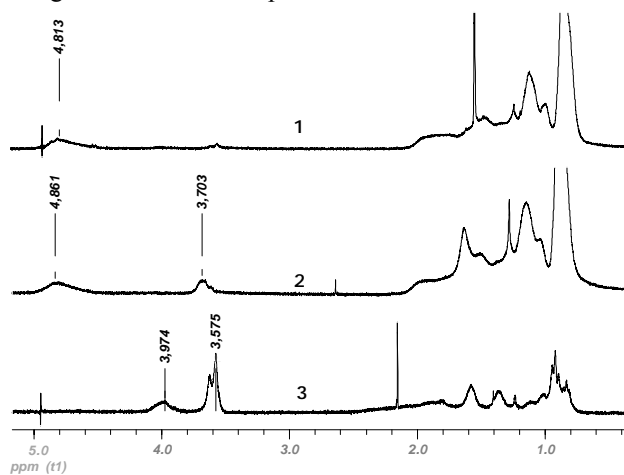


Fig. 1. ¹H-NMR spectra of VeoVa containing copolymers in CDCl₃: 1 – homopolymer; 2 – VeoVa:MMA:AR = 76:19:5 mol.%, 3 – VeoVa: MMA:BA:AR = 9:61:25:5 mol.% (monomeric units in a copolymer)

Adhesive coating technique

The supporting silk fabric was coated with the adhesive by casting a thin layer of the adhesive solution onto a teflon-coated fabric. When the film dried, the teflon-coated fabric was turned over, spread on the supporting fabric and heat-sealed with a hand-held iron. Then the

teflon-coated fabric was peeled off from the supporting fabric. The supporting fabric coated in this way was then adhered to the object by heat-sealing it with a spatula iron. The adhesive films prepared by this method were exposed to UV irradiation and used for evaluation of optical properties (blue dyed silk) and ATR-FTIR spectroscopy measurements (white silk). The thickness of the films was between 0.05 and 0.09 mm.

For all other tests, thick layers of the solution were cast on a polyethylene sheet and the films formed were detached after drying. These “free” films were exposed to artificial ageing conditions and used for pH and solubility tests.

Monitoring of accelerated ageing

The processes of ageing in the films were accelerated by UV irradiation following the established protocols [16, 17]. The ageing chamber was equipped with a battery of twenty low-pressure mercury fluorescent tubes, EVERSUN L40/79K (Osram), emitting radiation in the 310–410 nm spectral range with a total power of 800 W. The temperature in the chamber did not exceed 35 °C and the relative humidity was 40% RH. The duration of accelerated ageing was 2, 4, 8, 16, 32 days.

FTIR spectra were recorded with a Perkin–Elmer Spectrum BX spectrometer. The absorbance (A) spectra were recorded as attenuated total reflectance spectra from the adhesive film on the silk supporting fabric. For this purpose the ATR accessory with a ZnSe crystal was employed. The difference spectra were calculated by subtracting the spectrum of a sample of the adhesive film from the spectrum of an aged sample ($A_{\text{aged sample}} - A_{\text{control}}$).

Colour changes of the films were measured using a Spektrotron colorimeter equipped with the CIE Standard Illuminant C, which represents the average daylight with a correlating colour temperature of approximately 6770 K. The transmission spectra of the samples in the region from 380 to 700 nm were recorded by scanning them at 10 nm intervals. The colour difference ΔE in the CIE(Lab)* system was calculated according to the formula [18]:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2},$$

where ΔL^* (lightness-darkness difference) = $L^*_{\text{aged}} - L^*_{\text{unaged}}$;
 Δa^* (redness-greenness difference) = $a^*_{\text{aged}} - a^*_{\text{unaged}}$;
 Δb^* (yellowness-blueness difference) = $b^*_{\text{aged}} - b^*_{\text{unaged}}$.

The acidity (pH) was measured using a portable pH-330/SET pH-meter (WTW) equipped with a Sen TixMic41 combined measuring electrode. The solutions were prepared as described [19]: 0.4 g of a shredded film was extracted with 8 ml of distilled water for 72 h under normal conditions. The solubility of the adhesive films in acetone, ethyl acetate, chloroform and benzene was tested.

RESULTS AND DISCUSSION

The copolymers used as adhesives for textiles should meet some requirements. These copolymers should co-

ver a silk fabric with a flexible smooth film which must not affect the softness, flexibility, texture and colouring of the textile. A too rigid and insufficiently flexible film tends to shrink and corrugate the silk fabric which can lose its original shape. A too sticky surface of the adhesive film is not suitable either. An essential feature of a copolymer film is adhesion which is related mainly to the units of acrylic or methacrylic acid present in the macromolecules of copolymers [20]. The adhesive films should be UV resistant, not yellow under ageing and remain soluble enabling the further conservation and restoration of textile artefacts.

1. Copolymerization of VeoVa and acrylates in solution

In order to improve the ageing resistance of vinylacetate–acrylate adhesive films used in the conservation of museum textiles, the units of vinyl acetate in the copolymer were replaced by the units of vinyl neodecanoate. VeoVa units should impart an excellent chemical and UV resistance, add steric bulk to the polymer providing protection to less stable monomeric units [13] as well as to provide a “plasticizing effect” to the main chain. The latter effect is related to the glass transition temperature which is lower for VeoVa homopolymer ($T_g = -3$ °C) than for VA homopolymer ($T_g = 32$ °C) [21].

The comonomers were chosen in such a way that the effect of flexibility imparted by VeoVa units was compensated by more rigid units of MMA or EMA (T_g of the homopolymers of MMA and EMA are high, 105 °C and 65 °C, respectively [15, 21]). However, the terpolymers synthesized from the VeoVa–MMA–AA or VeoVa–EMA–AA monomer mixtures, irrespective of the monomer feed composition, were glassy and rigid, demonstrating the features inadequate for the conservation of textiles.

It is known [14, 15, 21] that the glass transition temperature of polymers containing monosubstituted monomeric units increases with the bulkiness of a substituent. On the other hand, longer n-alkyl side chains decrease T_g due to the internal “plasticizing effect” on the main chain. BA or BMA were used as comonomers decreasing T_g and increasing the elasticity of the terpolymers (T_g of poly-BA and poly-BMA is -54 °C and 20 °C, respectively). Both types of terpolymers, VeoVa–BMA–AA and VeoVa–BA–AA were in a rubbery-elastic state. However, the surface of the terpolymers was sticky, which made the application of these adhesives for the conservation of textiles impossible. Though the homopolymer of acrylic acid is glassy ($T_g = 106$ °C), the amount of AA units in terpolymers is too low (up to 5%) to affect the elasticity of the terpolymers.

It was presumed that a simultaneous presence of BA and MMA units in copolymers should provide the right ratio of elasticity and rigidity, making these copolymers applicable for textile conservation. The best results were achieved using copolymers synthesized from the initial monomer feeds VeoVa : MMA : BA : AA = 35 : 30 : 30 : 5 mol% and VeoVa : MMA : BA : AA = 25 : 30 : 40 : 5 mol%, named thereafter as VeoVa-35 and VeoVa-25, respectively.

These tetrapolymers are able to form flexible and transparent films on a silk fabric as well as on hydrophobic surfaces, and the adhesion of the films is good. The intrinsic viscosity of the tetrapolymers is relatively low ($[\eta] = 0.2\text{--}0.3$ dl/g), indicating a moderate or low average molecular weight of these polymers.

Since MMA is much more reactive than VA ($r_{VA} = 0.026$ and $r_{MMA} = 24.025$ [14, 15, 22]), the same tendency is expected in the pair of comonomers VeoVa–MMA [13]. The reactivity ratios of the comonomers MMA and BA also differ ($r_{MMA} = 1.871$ and $r_{BA} = 0.291$ [13, 22]), but the difference is not as drastic as in the above pair. The low reactivity ratio of VeoVa in the radical copolymerization with (meth)acrylates results in random copolymers with a relatively low content of VeoVa units in the copolymers (Table 1). Moreover, these copolymers are expected to be chemically heterogeneous, since in the initial stage of copolymerization macromolecules are to be enriched by MMA segments, while at a high conversion of the monomers when more reactive (meth)acrylates are almost consumed, VeoVa segments can compose a considerable part of macromolecules. For example, the five-hour copolymerization of four-component monomer feeds containing 35 mol.% of VeoVa resulted in tetrapolymers containing 9 mol.% of VeoVa units (Table 1). A higher amount of VeoVa units (15 mol.%) in the average copolymer composition was determined when the time of the reaction was prolonged up to 10 hours. It is worth noting that the introduction of even a small amount of AA into the monomer feed (5 mol.%) results in a considerable increase of VeoVa units.

2. Filming of VeoVa-containing copolymers on textiles

The ability of VeoVa–acrylate copolymers to form smooth films on supporting silk fabric and the possibility to apply them as adhesives for textile conservation were assessed. It was determined that VeoVa homopolymer and copolymers containing over 80 mol.% of VeoVa units penetrated into the silk fiber and did not form smooth films on the fabric surface. The VeoVa–MMA–AA and VeoVa–EMA–AA copolymers, irrespective of their composition, tended to form rigid and fractured films on silk fabric. The VeoVa–BA–AA and VeoVa–BMA–AA copolymers did not form smooth coatings, penetrated the silk fabric and coupled the silk yarns in aggregations, which

resulted in colour change of the dyed silk fabric. The adhesion of films to silk fabric was certainly weak. Transparent and flexible films of these copolymers, however, were formed on hydrophobic surfaces.

The compositions of tetrapolymers VeoVa–MMA–BA–AA containing 9–15 mol.% of VeoVa units formed flexible and transparent films on silk fabric as well as on hydrophobic surfaces. The adhesion of the films to silk fabric was good enough in this case (Table 2). An increase in MMA units in the tetrapolymers led to less flexible films coating the silk fabric and shrank it. The best results from the point of adhesive application were achieved using the copolymers VeoVa-35 and VeoVa-25. It is worth noting that the compositions without segments of acrylic acid do not form a smooth flexible film on the surface of the fabric; moreover, the adhesive itself forms a web of polymer fibrils at the intersections of silk yarns. Thus, the presence of the units of AA is essential for obtaining smooth highly adhesive films on the surface of silk fabric.

3. Accelerated ageing of VeoVa containing copolymers

The ageing resistance of both VeoVa tetrapolymers VeoVa-35 and VeoVa-25 under UV irradiation was compared with the stability of poly(vinyl acetate-acrylate) copolymer A-45K [7, 8] as well as with the stability of plain silk fabric under the accelerated ageing conditions (Fig. 2). The changes of the films during UV irradiation were evaluated by measuring the optical properties, acidity,

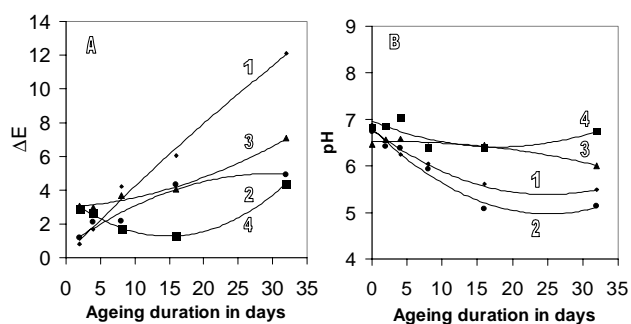


Fig. 2. Colour difference ΔE (a) and pH of the extract (b) of the blue coloured support silk fabric uncoated (1) and coated (2–4) by adhesive films versus the duration of accelerated ageing. The supporting silk fabric was coated with A-45K (2), VeoVa homopolymer (3) and VeoVa-35 copolymer (4)

Table 1. Composition of VeoVa copolymers synthesized at 70 °C using 0.2% of AIBN

Monomers	Composition of initial monomer feed, mol.%	Composition of copolymer, mol.%	Conversion, %
<i>Terpolymers</i>			
VeoVa:MMA:AA	35 : 60 : 5	12 : 83 : 5	17
VeoVa:MMA:BA	35 : 35 : 30	5 : 55 : 40	18
VeoVa:BA:AA	35 : 60 : 5	19 : 76 : 5	36
<i>Tetrapolymers</i>			
VeoVa:MMA:BA:AA	25 : 30 : 40 : 5	11 : 45 : 39 : 5	27
VeoVa:MMA:BA:AA, $\tau = 5$ hours	35 : 30 : 30 : 5	9 : 61 : 25 : 5	26
VeoVa:MMA:BA:AA, $\tau = 10$ hours	35 : 30 : 30 : 5	15 : 46 : 34 : 5	42

Table 2. Features of VeoVa tetrapolymer films coating various surfaces

Abbreviation	Composition of the initial monomer feed, mol.%				Film on a hydrophobic surface	Film on a plain silk fabric	“Free” film
	VeoVa	MMA	BA	AA			
VeoVa-35	35	30	30	5	Flexible, non-fractured	Flexible and smooth	Transparent and flexible
	35	40	20	5	Does not shrink	Tends to shrink the fabric	Transparent, insufficiently flexible
	35	50	10	5	Shrinks	Tends to coil the silk	Fragile with orange-peel effect
VeoVa-25	25	30	40	5	Flexible, non-fractured	Flexible and smooth	Transparent, glossy and moderate flexible
	25	40	30	5	Fractured	Tends to shrink the fabric	Transparent, non-fractured, but insufficiently flexible
	25	50	20	5	Fractured	Tends to shrink the fabric	Transparent and rigid

solubility, and analyzing the infrared absorption spectra of the films covering the plain silk fabric.

The copolymer films exposed to an accelerated light ageing tended to change their optical properties. The colour difference of the films covering the silk fabric coloured in blue, increases marginally, which is in contrast to the plain silk fabric which changes colour much faster. Thus, the film plays a preventive role in the protection of the silk fabric. The colour difference ΔE of the homopolymer film keeps its value nearly constant up to the 16th day of ageing, but later it tends to grow bypassing the corresponding value of the film of A-45K. The film of VeoVa-35, in contrast to other films, tends to fade in the first stage of ageing; the further ageing up to 32 days results in a moderate increase of the colour difference. The measurements of pH of the film extracts complement and confirm the data of the optical measure-

ments. The changes in pH of the films of VeoVa-35 are minimal and pursue the curve of colour changes. On the contrary, the acidity of the extract of the film of A-45K drops much more considerably from the pH value of 6.74 to 5.08. The films of VeoVa polymers preserved their solubility in acetone for a long time. They became partially insoluble starting from the 16th day of ageing in the case of the homopolymer and from the 32nd day of ageing in the case of VeoVa-35. Thus, a conclusion can be made that VeoVa units containing copolymers are relatively more stable to UV irradiation than those containing vinyl acetate units.

FTIR spectra of the copolymers reflect the main chemical changes occurring under the UV irradiation of the adhesive films (Fig. 3). The absorption bands characteristic of methyl/methylene vibrational modes were found to be sensitive to ageing. The absorption bands

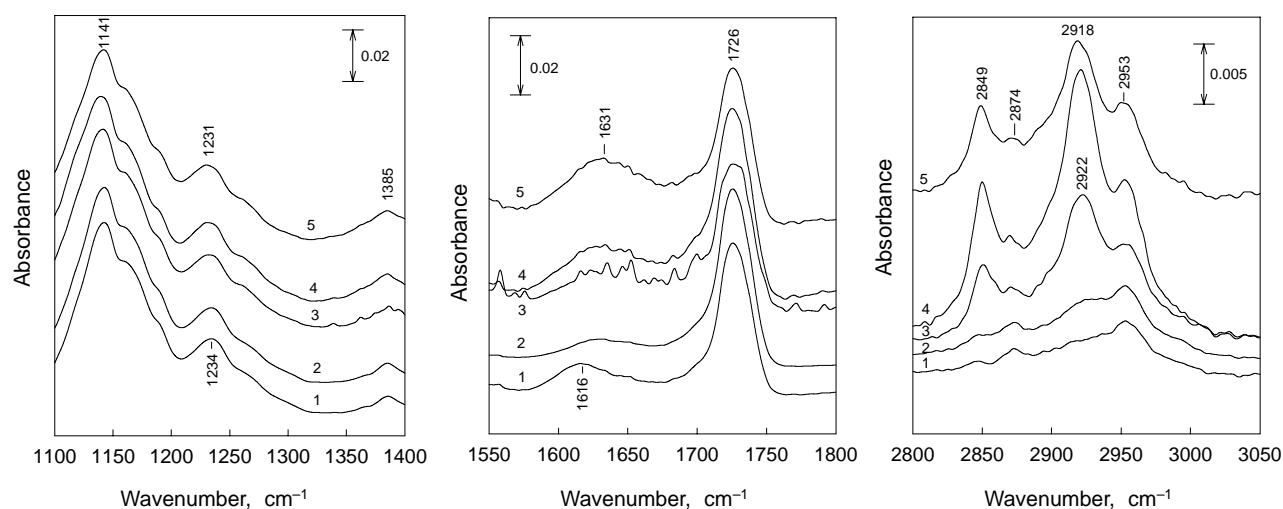


Fig. 3. FTIR spectra of the films of the aged adhesive VeoVa-35 recorded in the 1100–1400, 1550–1800 and 2800–3050 cm^{-1} spectral regions. The duration of ageing under UV irradiation was 0 (1), 2 (2), 8 (3), 16 (4) and 32 (5) days. Spectra are arbitrarily shifted along the ordinate

associated with stretching asymmetric and symmetric vibrational modes of methyl groups at 2953 and 2874 cm^{-1} , respectively, dominate in the spectrum of a non-irradiated copolymer film. The intensity of these bands slightly decreases when the film of copolymer undergoes the UV irradiation, and vibrational modes of methylene groups at 2922 and 2851 cm^{-1} become predominant. The changes in the methyl/methylene spectral region are confirmed by the band at 1385 cm^{-1} which corresponds to the deformation $\delta(\text{CH}_3)$ vibrations of the methyl group. The intensity of this band under irradiation decreases, while the width increases from 27 up to 34 cm^{-1} (Table 3). The broadened band of the methyl deformation vibrations mode indicates an increase in heterogeneity of the environment around the CH_3 groups.

Table 3. Changes in width of characteristic bands during artificial ageing

Frequency, cm^{-1}	Assignment	Width, cm^{-1}				
		Initial	2 days	8 days	16 days	32 days
1726	$\nu(\text{C}=\text{O})$	26	27	28	28	26
1385	$\delta(\text{CH}_3)$	27	27	27	30	34
1141	$\nu(\text{C}-\text{O}-\text{C})$	68	70	70	70	70

The absorption bands at 1726 and 1141 cm^{-1} associated with stretching vibrational modes of carbonyl $\nu(\text{C}=\text{O})$ and ether $\nu(\text{C}-\text{O})$ groups, respectively, remain practically constant: there is no shift in the position of the bands, and there are no significant changes in the intensity and width of the bands (Table 3). The progressive decrease of the methyl absorption bands in the region 2800–3000 cm^{-1} may be attributed to the loss of low-molecular-weight compounds formed during the irradiation, or to the appearance of new absorption bands characteristic of the silk fibroin. The absorption associated with protein is confirmed by the band at 1631 cm^{-1} attributed to the amide I band.

As it is obviously seen from Table 3, the width of the $\delta(\text{CH}_3)$ band broadens during the whole irradiation period; thus, this feature can not be chosen as an internal standard for normalizing the subtraction procedure in order to calculate difference spectra. The least changing absorption band is at 1141 cm^{-1} which is attributed to the stretching $\nu(\text{C}-\text{O})$ vibration of the MMA groups; this band could be considered as an internal standard for the preparation of difference spectra.

The difference spectra normalized according to the internal standard at 1141 cm^{-1} , show the formation of new functional groups or disappearance of the former groups (Fig. 4). For instance, the formation of ketone group is evidenced [9, 10] by a shift of the carbonyl group to 1716 cm^{-1} which occurred by the 16th day of ageing.

After 32 days of ageing new, positive going band at 1645 cm^{-1} instead of the carbonyl $\nu(\text{C}=\text{O})$ vibrational mode appeared in the difference spectrum. We attributed these vibrations to amide I mode originated from the

stretching $\nu(\text{C}=\text{O})$ vibration of the peptide group whose frequency depends on the hydrogen-bonding and coupling along the protein chain; therefore this band is sensitive to the protein secondary structure [23–28]. It is generally accepted [23–26] that *Bombyx mori* silk fibroin has three major conformations in its solid state, which are random coil, silk I structure, and β -sheet (or silk II) structure. Crystallinity of fibroin is associated with β -sheet secondary structure represented by the amide I bands at 1638 and 1629 cm^{-1} [23–28]. The absorption band at 1645 cm^{-1} observed in our case is associated with an unordered α -helix conformation [28, 29], probably due to the silk fibroin destruction under the UV irradiation. The next positive vibrational mode at 1508 cm^{-1} can be attributed to symmetric $\delta_s(\text{NH}_3^+)$ deformation vibrations [30] characteristic of the formation of ionized amine $-\text{NH}_3^+$ due to bonding of $-\text{NH}_2$ group from the fibroin with acidic

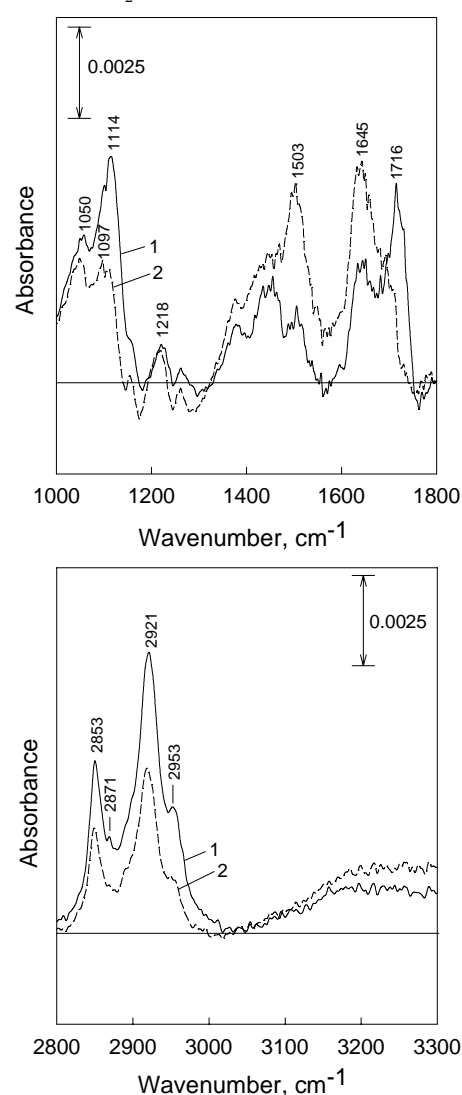


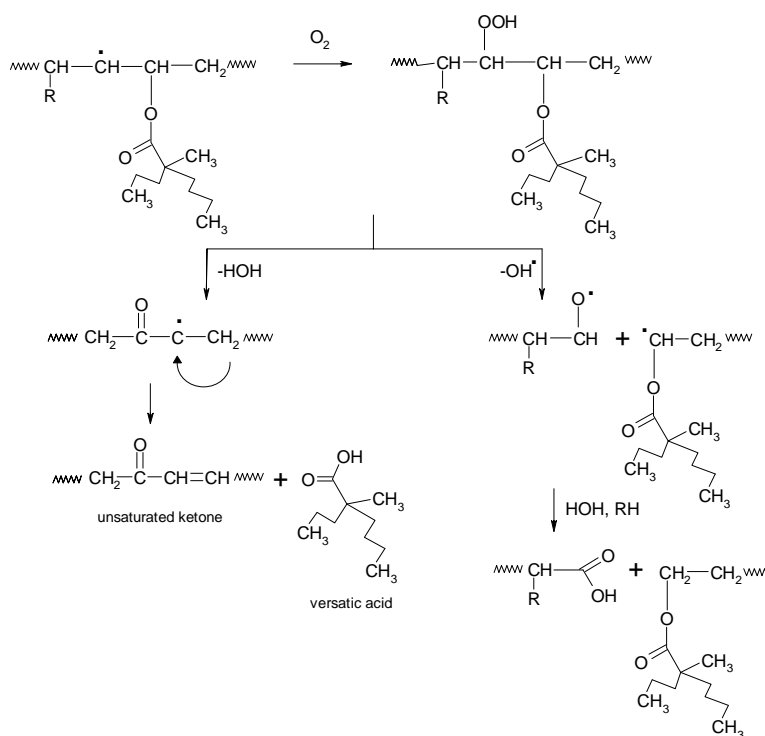
Fig. 4. Difference spectra of the films of the aged adhesive VeoVa-35 recorded in the 2800–3500 cm^{-1} and 1550–1800 cm^{-1} spectral regions. The difference spectra were normalized according to the stretching $\nu(\text{C}-\text{O})$ vibrational band at 1141 cm^{-1} . The duration of ageing under UV irradiation was 16 (1) and 32 (2) days

carboxyl group from the copolymer. It should be noted that this band overlaps with the amide II band at 1548 cm^{-1} associated mainly with the combination of the N–H bending and the C–N stretching vibrations of the –CO–NH– group in its *trans*-form [26, 28]. The other two positive going absorption bands located at 1050 and 1097 cm^{-1} and associated with the stretching $\nu(\text{C–O})$ vibrations of alcohols, can be assigned to the vibrations of the hydroxyl groups present in amino acids of silk fibroin and, possibly, to the new derivatives of the copolymer, for example, vinyl hydroxyl groups.

In the range of high frequency, the intense positive features are observed at 2853 and 2921 cm^{-1} , attributed to the symmetric stretching $\nu_s(\text{CH}_2)$ and asymmetric stretching $\nu_{as}(\text{CH}_2)$ vibrational modes of the methylene group, respectively. These new features dominate against the methyl group stretching vibrational modes at 2953 and 2871 cm^{-1} (asymmetric and symmetric, respectively). Thus, the difference spectra clearly indicate a decrease of the VeoVa segments containing methyl groups, as well as an increase of segments attributed to other compounds containing methylene groups, e.g., silk fibroin. Broad medium intense absorption band at $3100\text{--}3300\text{ cm}^{-1}$ can be attributed to the stretching vibrational modes of both amine or hydroxyl groups of silk fibroin as well.

Therefore, the difference spectra (Fig. 4) revealed chemical changes in macromolecules of the copolymer VeoVa-35 and confirmed the presumption that the film of the copolymer lost its integrity. The loss of integrity resulted in partial transparency of the film enabling to increase the absorption bands attributed to the amide and methylene groups of silk fibroine.

The copolymers based on VeoVa units as in the case of vinyl acetate [9] should age according to the common mechanism of auto-oxidation. The process of oxidation caused by high energy UV irradiation takes place through the consumption of oxygen and formation of unstable hydroperoxides at the β -position to the VeoVa group (Scheme 2). The subsequent decomposition of hydroperoxides leads to the rupture of the lateral VeoVa groups (Norrish I type process) or cleavage of the main chain (Norrish II type process). The first process leads to the formation of unsaturated ketones and versatic acid. Particularly, film yellowing could be related to the formation of unsaturated ketones. Versatic acid is non-volatile and remains integrated in the film of the copolymer. The second Norrish II type process is associated with a breakdown of unstable hydroperoxides and the formation of active hydroxyl radicals which can cleave the main chain at any position. The fragmented macroradicals with the terminal aldehyde groups are usually oxidized to carboxyl compounds. Other fragmented macro-



Scheme 2. Photooxidation of a VeoVa copolymer leading to the rupture of the lateral VeoVa group or to fragmentation of the copolymer main chain

radicals are able to abstract hydrogen from water or adjacent macromolecules and form saturated polymeric or oligomeric structures.

It is not evident which type of the process is predominant. Probably, the rupture of the lateral VeoVa groups prevails (Norrish I type process) in the initial stage of ageing while later the breakdown of unstable hydroperoxides to active hydroxyl radicals leads to fragmentation of the main chain (Norrish II type process). The fragmentation of the main chain of the copolymer could be responsible for acidification and loss of integrity of the irradiated films.

CONCLUSIONS

The units of vinyl acetate in poly(vinyl acetate–acrylate) copolymer were replaced by bulky units of vinyl neodecanoate 10 (VeoVa) in order to improve the ageing resistance of the adhesive layers used in lining of museum textiles. Several VeoVa terpolymers and tetrapolymers with various (meth)acrylates were synthesized and studied.

The films of VeoVa terpolymers containing MMA or EMA units were insufficiently elastic and had ruptures, while VeoVa terpolymers containing BA or BMA units tended to soak into silk fabric and stick to silk yarn resulting in colour change of the silk fabric. Tetrapolymers containing the right ratio of the units of MMA and BA met the requirements for textile adhesives. From the point of coating features, most suitable are tetrapolymers with the composition close to VeoVa : BA : MMA : AA = 15 : 35 : 45 : 5 mol.%.

Contrary to expectation, bulky units of VeoVa demonstrated neither excellent UV resistance nor provided protection to the adjacent acrylic segments in copolymers. VeoVa-containing copolymers underwent ageing according to the common mechanism of auto-oxidation, leading to a rupture of the lateral VeoVa groups in the initial stage of the process and cleavage of the polymer main chain in further stages of artificial ageing. Nevertheless VeoVa copolymers are relatively more resistant to UV irradiation than those containing vinyl acetate units and can be used as a support for museum textiles.

ACKNOWLEDGEMENT

We gratefully acknowledge Dr. Habil. Gediminas Niaura for his help in preparing ATR-FTIR and difference FTIR spectra and for useful consultations.

Received 30 June 2006

Accepted 11 July 2006

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MUZIEJINĖS TEKSTILĖS RESTAURAVIMUI SIŪLOMŲ VINILNEODEKANOATO KOPOLIMERŲ PLĖVELIŲ SUDARYMO IR SENĖJIMO YPATYBIŲ TYRIMAS

Santrauka

Ilgą laiką muziejinė tekstilė buvo restauruojama vinilacetato (VA)–akrilato kopolimerų klijais, padengiančiais šilkinį audinį tolygia elastinga plėvele, kuri, deja, natūraliai sensta dienos šviesoje. Pažeitus jautrią senėjimui VA grandį šakota vinilneodekanoato 10 (VeoVa) grandimi, tikėtasi gauti stabilius apšvitai ir atsparius šarminei hidrolizei kopolimerus. Sintetinių kopolimerų sudėtis buvo įvertinta, nustatant jų rūgščių skaičių ir kiekybiškai analizuojant ¹H-BMR spektrus. Tinkamiausios kopolimerų kompozicijos pasirinktos, atsižvelgiant į jų gebėjimą sudaryti ant šilkinio audinio tolygią ir elastingą plėvelę. VeoVa kopolimerų plėvelių ant šilko stabilumas UV spinduliuotės poveikiui buvo įvertintas matuojant jų optinį pralaidumą, ekstrakto pH, tirpumą ir užrašant ATR-FTIR spektrus. Kopolimero cheminės struktūros pokyčiai buvo įvertinti, analizuojant skirtuminius FTIR spektrus, gautus atėmus kontrolinės plėvelės spektrą iš tiriamojo (pasenusio) kopolimero spektro. Skirtuminiai spektrai atskleidė autooksidacinį radikalinių senėjimo mechanizmą, kurio metu pirmojoje sendinimo stadijoje sparčiau vyksta šoninės VeoVa grupės atskilimo reakcija, susidarant nesotiems ketonams ir versato rūgščiai. Tolimesniame senėjimo procese susidaro aktyvūs hidroksilo radikalai, pajėgūs skaldyti kopolimero makromolekulę į atskirus fragmentus, todėl kopolimero plėvelė praranda vientisumą. Nepaisant to, VeoVa kopolimerai santykinai atsparesni UV švitinimui, negu analogiški vinilacetato kopolimerai, todėl gali būti naudojami muziejinės tekstilės restauravimui.