Advanced organic-inorganic hybrid fillers as functional additives for poly(vinyl chloride)

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Abstract: Functional hybrid fillers (kraft lignin conjugated with Sylobloc® 41 silica) were obtained using a process of mechanical grinding of precursors. The products underwent comprehensive physicochemical and dispersive-morphological analysis. The organic-inorganic fillers have good homogeneity and a relatively high surface area. Composites of rigid poly(vinyl chloride) as a matrix with these specific dual fillers were produced in molten state. Data on the processing properties of the blends show the beneficial impact of fillers on gelation time. The presence of lignin/silica fillers strongly influences the thermal stability of PVC as well as Vicat softening temperature.

Keywords: lignin/silica hybrid filler, poly(vinyl chloride), physicochemical and structural properties, processing properties.

Zaawansowane organiczno-nieorganiczne napełniacze hybrydowe jako funkcjonalne dodatki do poli(chlorku winylu)

Streszczenie: Funkcjonalne napełniacze hybrydowe wytworzono przy użyciu ligniny krafta oraz krzemionki Sylobloc® 41, z wykorzystaniem procesu mechanicznego rozdrabniania prekursorów. Otrzymane produkty poddano analizie fizykochemicznej i dyspersyjno-morfologicznej. Wytworzone organiczno-nieorganiczne napełniacze hybrydowe charakteryzowały się jednorodną strukturą oraz rozwiniętą powierzchnią właściwą. Na bazie poli(chlorku winylu) i uzyskanych napełniaczy hybrydowych otrzymywano kompozyty w stanie stopionym. Oznaczone właściwości przetwórcze wskazują na korzystny wpływ użytych napełniaczy na czas żelowania mieszanek. Obecność układu hybrydowego lignina/krzemionka w istotnym stopniu oddziałuje także na stabilność cieplną PVC oraz jego temperaturę mięknienia wg Vicata.

Słowa kluczowe: napełniacz hybrydowy lignina/krzemionka, poli(chlorek winylu), właściwości fizykochemiczne i strukturalne, właściwości przetwórcze.

Lignin is one of the world's most common biopolymers, and is also a renewable and eco-friendly raw material [1–6]. It is a byproduct in the chemical and mechanical conversion of wood cells. This biopolymer is composed of three main alcohols as monomers: *p*-coumaryl, coniferyl, and sinapyl [1, 2, 4–6]. The contents of the monomers depend on the plant species.

The literature contains many reports of applications of this byproduct, especially in polymer processing [1, 3, 5, 7–10]. Lignin is a renewable source which is easily degradable in the natural environment, and this gives its potential for use in polymer blends [5, 11]. This biopolymer can be used as a plasticizer of poly(vinyl chloride) [12–15]. Strong hydrogen bonds are known to be formed between lignin and poly(vinyl chloride), but only at low biopolymer loading. This is due to the tendency of lignin molecules to associate, which is stronger than the formation of bonds with PVC [13–16]. PVC/lignin materials have lower glass temperature than pure lignin [14, 15] and can absorb UV radiation [14]. The addition of lignin to PVC can also improve the elongation at break, but the tensile strength will decrease [15]. The recycling of polymers is currently a very important factor, and may be achieved by selective flotation. The use of lignin as a plasticizer of PVC or poly(ethylene terephthalate) (PET) also helps in this recovery procedure [17]. This biopolymer can also be applied in polyolefin blends such as polypropylene (PP) and polyethylene (PE) [1, 5, 10, 18, 19]. Bozsódi *et al.* [10] reported that the addition of lignosulfonates to maleic anhydrate grafted polypropylene matrix leads to better dispersion of the filler particles and improved mechani-

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cal strength (compared with tests using pure polypropylene). The addition of lignosulfonates also affects the effectiveness of nucleation of PP. In turn, Borysiak *et al*. [19] tested the effect of silica/lignin hybrid fillers on growth of the crystalline β phase, showing that the largest content of that phase occurred in the system filled with a hybrid material with a silica : lignin ratio = 20 : 1 (wt/wt). Similar tests have been carried out for a composite system based on PLA [20]. The authors noted that the presence of hybrid filler in the PLA matrix has an influence on the formation of a transcrystalline layer and therefore influences the supermolecular structure of the composites. They report that composites with silica and hybrid filler form a transcrystalline structure at the matrix/filler interface, whereas PLA and PLA/lignin composites form spherulites. The presence of silica in a hybrid filler restricts the formation of spherulites and is thus responsible for transcrystalline layer formation. Moreover, lignin/silica hybrid material is a filler capable of producing effective crystal nucleation of PLA [20]. PP forms with lignin immiscible blends such as lignin/poly(vinyl alcohol) [11]. The interactions between PP and the biopolymer may be improved by the activation of lignin with bromododecane, but this has a negative impact on the mechanical properties of the material [21]. Miscible lignin/polymer blends can be obtained with PET or poly(ethylene oxide) (PEO) [22].

Based on the results of our earlier research [23] it was noted that a composite with a PVC matrix and lignin/silica filler, composed of 20 parts by weight of kraft lignin to 100 parts of Syloid® 244 silica, produced in molten state, has a homogenous structure as well as beneficial processing and thermal properties. Silica as a component of the hybrid filler gives the most effective improvement in Young's modulus and softening temperature, while lignin causes significant increase in the thermal stability of PVC as the matrix of the composite.

The aim of our investigations was to determine the influence of a new generation of dual lignin/silica hybrid fillers, with various proportions of the two components, on the processing and structural properties of rigid poly(vinyl chloride).

EXPERIMENTAL PART

Materials

Hybrid fillers containing the amorphous silica Sylobloc® 41 (W.R. Grace Davison & Co., USA) and kraft lignin (Sigma Aldrich, USA) were produced using a mechanical method. The method of preparation of organic-inorganic hybrids is described in detail in our previous paper [23]. Three types of lignin/silica hybrid fillers with different contents of the components (1 : 5, 1 : 1 and 5 : 1 wt/wt) were introduced into a rigid PVC matrix, with respective filler concentrations of 2.5, 5.0, 7.5 and 10.0 wt %.

A PVC compound containing PVC S-61 Neralit (Spolana Anwil Group, Czech Republic), mixed with 4 wt % of the organotin stabilizer Patstab 2310 (Patcham, Netherlands) and 1 wt % of the paraffin wax Naftolube FTP (Chemson, Austria), was used as the matrix for the investigated composites.

Preparation of PVC composites

Before processing, all types of filler were dried at 105 °C for 3 h. The compositions of the PVC mixtures and their abbreviations as used in the text are given in Table 1.

In order to produce homogenous PVC composites, all mixtures were processed by means of a Brabender mixer equipped with a kneading chamber (Plasti-Corder Pl 2200-3, Brabender GmbH & Co., Germany) operating at a temp. of 190 °C. The rotational speed of the blades was 30 rpm, and the sample weight was 58 g. Processing was always continued until an equilibrium state of torque was achieved. The torque values were recorded as a function of time. Plastograms were used to analyze the maximum values of torque (M_X) and the time taken to reach those maximum values (t_X). The unfilled PVC dry blend was processed under similar conditions as a reference sample. All processed PVC materials were ground, and moldings with thicknesses of 2 mm and 4 mm were achieved by compression at a temp. of 180 °C. Samples cut from the moldings were used for investigation of Vicat softening temperature and of their mechanical properties. The processing properties (mass melt flow rate –

Table 1. Composition of the PVC-based composites

Sample name	Filler type	Filler content, wt %
PVC/A1	Lignin/silica hybrid (1 : 5, wt/wt)	2.5
PVC/A2		5.0
PVC/A3		7.5
PVC/A4		10.0
PVC/C1	Lignin/silica hybrid (1 : 1, wt/wt)	2.5
PVC/C2		5.0
PVC/C3		7.5
PVC/C4		10.0
PVC/E1	Lignin/silica hybrid (5 : 1, wt/wt)	2.5
PVC/E2		5.0
PVC/E3		7.5
PVC/E4		10.0
PVC	–	0.0
PVC/S1	Silica	2.5
PVC/S2		5.0
PVC/S3		7.5
PVC/S4		10.0
PVC/L1	Lignin	2.5
PVC/L2		5.0
PVC/L3		7.5
PVC/L4		10.0

MFR) and Congo red thermal stability were determined by means of milling of the composites.

During the kneading of PVC mixtures with silica, the same effect as described in [23] was observed, namely in the case of the PVC compound with 10 wt % silica evidence of degradation during mixing was observed, and investigations using that material were discontinued.

Methods of testing

Physicochemical evaluation of hybrid fillers

– Particle size distribution was determined using a Zetasizer Nano ZS (Malvern Instruments Ltd., UK) enabling measurement of particle diameters in the range 0.6–6000 nm (noninvasive backscattering technique, NIBS). The dispersive properties of the products were also determined with the use of a Mastersizer 2000 apparatus (0.2–2000 μm), also from Malvern Instruments Ltd., employing the method of laser diffraction.

– The surface morphology and microstructure of the lignin/silica hybrid fillers were examined on the basis of SEM images recorded from an EVO40 scanning electron microscope (Zeiss, Germany). Before testing, the samples were coated with gold for 5 s using a Balzers PV205P coater (Oerlikon Balzers Coating SA, Switzerland).

– Porous structure parameters of the hybrid fillers were obtained using the low-temperature nitrogen sorption technique. Measurements were made on an ASAP 2020 instrument (Micromeritics Instrument Co., USA).

Properties of PVC composites

– Static thermal stability tests using the Congo red method were carried out at 190 °C in accordance with the ISO 182-1:1990 standard.

– Tests of Vicat softening temperature were performed in accordance with PN-EN ISO 306:2006, using 10 mm × 10 mm × 4 mm specimens. The measurements for each type of sample were carried out three times, in accordance with the requirements of the standard.

– Melt flow rate testing was performed using an MFR indexer (Dynisco D4004DE, USA) according to the ASTM D 1238 standard. The measurements were performed at barrel temp. 190 °C using a capillary die with length 8 mm and diameter 2.095 mm.

– Tensile properties were determined using a Zwick Roell Z010 testing machine (Zwick GmbH & Co. KG, Germany), at a strain rate of 20 mm/min, at room temperature, in accordance with the PN-EN ISO 527-1 standard, using specimens of type 1BB, 2 mm in thickness. For each PVC material, 10 specimens were subjected to the tensile procedure.

– Microscope observations were used to assess the structure of PVC composites and the homogeneity of distribution of filler particles in the PVC matrix. The microstructure was observed by scanning electron microscopy (Zeiss EVO40, Germany). The samples were broken in liquid nitrogen, and before being placed in the chamber of the microscope they were coated with gold for 5 s using a Balzers PV205P coater.

RESULTS AND DISCUSSION

Properties of hybrid fillers

Table 2 presents the results obtained for the dispersive properties and porous structure parameters of lignin, silica, and the lignin/silica hybrid fillers.

The hybrid systems exhibited a tendency towards the formation of aggregates, and consequently agglomerates, with increasing content of kraft lignin per 100 parts by weight of silica. As can be seen from the results obtained using the Zetasizer Nano ZS apparatus, lignin/silica hybrid materials tended to form larger agglomerates of particles. A similar conclusion was drawn from the particle size parameters given by the Mastersizer 2000 analyzer, shown in Table 2. Thus the hybrid fillers contained pri-

Table 2. Dispersion data for kraft lignin, Sylobloc 41® silica, and the lignin/silica hybrid fillers

Sample name	PSD from Zetasizer Nano ZS, nm	Particle diameter from Mastersizer 2000, μm				Porous structure parameters		
		d(0.1)	*d*(0.5)	*d*(0.9)	*D*[4.3]	BET surface area, m²/g	Total volume of pores, cm³/g	Mean size of pores, nm
Silica	825–1990 3580–5560	3.5	17.3	25.4	17.9	316	0.20	2.7
Lignin	91–220 825–1110 1990–5560	2.9	23.4	38.9	24.5	1	0.01	11.4
Lignin/silica (1 : 5, wt/wt)	122–825 1990–4145	3.2	18.4	27.8	19.1	241	0.14	2.9
Lignin/silica (1 : 1, wt/wt)	106–955 2305–4800	3.1	19.6	27.9	20.2	94	0.04	3.3
Lignin/silica (5 : 1, wt/wt)	91–825 3580–5560	3.1	19.8	28.9	20.5	42	0.02	3.7

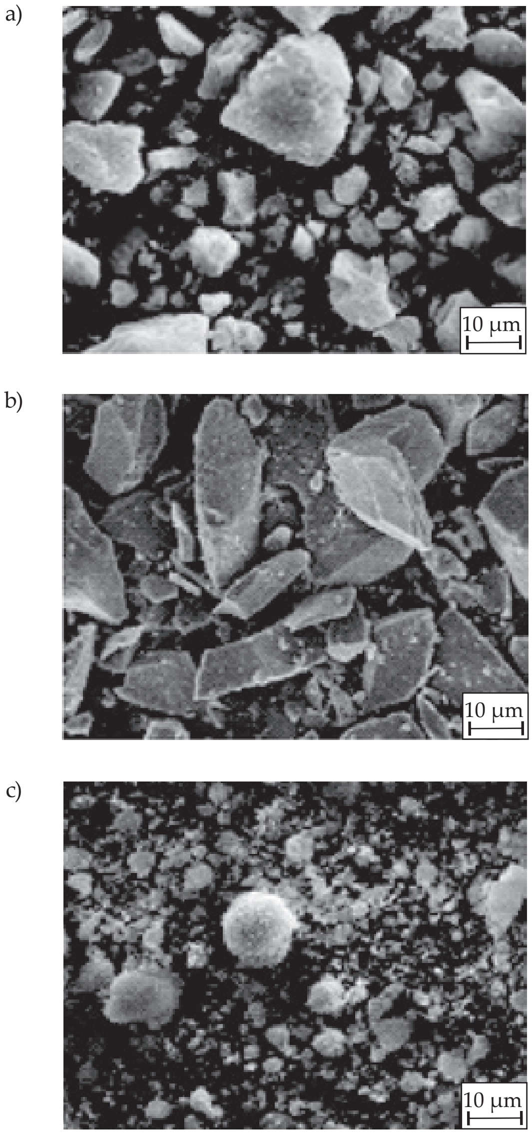

Fig. 1. SEM images of: a) Sylobloc® 41 silica, b) kraft lignin, c) lignin/silica hybrid filler (1 : 1 wt/wt)

mary particles showing a tendency towards the formation of aggregates (< 1 μm) and agglomerates (> 1 μm).

The above conclusions were corroborated by the SEM image presented in Fig. 1c (lignin : Sylobloc® 41 hybrid filler = 1 : 1 wt/wt). The formation of larger particle structures is fully to be expected. It follows from the structure and morphology of Sylobloc® 41 (Fig. 1a) and the structure of lignin macromolecules (Fig. 1b).

Investigation of the porous structure parameters involved determination of the values of BET surface area, total pore volume, and mean size of pores. The BET surface area value for the silica Sylobloc® 41 is 316 m^2/g, while the total pore volume and pore size are 0.20 cm^3/g and 2.7 nm, respectively. The lowest value of BET surface area (1 m^2/g) was recorded for kraft lignin. Interestingly, for the adsorption of substances on the surface of the hybrid materials it is not BET surface area that is crucial, but the nature and quantity of various functional groups present on the surface of the biopolymer. A very interesting, although expected, observation concerned the change in porous structure parameters depending on the lignin content in the materials. The higher the content of biopolymer, the lower the BET surface area. Similar behavior was found for the parameters of total pore volume and average size of pores – the differences are shown in Table 2.

Properties of PVC composites

The curves showing torque as a function of kneading time for all PVC blends with silica, lignin, and hybrid fillers are generally similar, and are typical for rigid PVC, reflecting the changes in the morphological structure of primary PVC grains which are related to the effect of gelation during processing [24–26]. However, the type and content of fillers are observed to have an effect on the fusion characteristics of the PVC/silica, PVC/hybrid, and PVC/lignin composites, melted in the Brabender torque rheometer. Table 3 summarizes the influence of the fillers on the value of maximum torque and the time taken to reach that value.

Based on the data presented in Table 3 it may be stated that the addition of as little as 2.5 parts by weight of silica results in a significant increase in torque, up to 60 Nm. It may be assumed that this effect is related to an increase in the friction of hard particles of silica against silica particles and/or PVC grains, which results in greater resistance of the processed material to the rotors. The lignin/silica fillers with component ratios of 1 : 5 and 1 : 1 wt/wt also cause an

Table 3. Effects of silica, lignin, and hybrids on the fusion properties of the PVC composites

Sample name	M_X, Nm	t_X, min
PVC/A1	56.9	1.47
PVC/A2	65.4	0.87
PVC/A3	74.7	0.88
PVC/A4	78.4	0.97
PVC/C1	51.1	1.83
PVC/C2	59.8	1.38
PVC/C3	71.0	0.95
PVC/C4	72.2	0.95
PVC/E1	44.7	1.97
PVC/E2	46.4	1.73
PVC/E3	48.3	1.47
PVC/E4	50.1	1.57
PVC	46.3	3.30
PVC/S1	62.1	1.50
PVC/S2	71.3	1.67
PVC/S3	76.4	1.75
PVC/S4	–	–
PVC/L1	47.5	1.83
PVC/L2	47.8	1.73
PVC/L3	46.1	1.55
PVC/L4	44.9	1.43

increase in the maximum torque of the PVC: the value of M_X increases with an increase in the content of a given type of filler in the composite. A high M_X value obtained for the above described composite (above 70 Nm when the filler content is greater than 5 wt %) is disadvantageous from the point of view of the processing technology, due to the very high mechanical workload of the processing machine.

An increase in the content of lignin in the hybrid filler (lignin : silica weight ratio 5 : 1 wt/wt) causes its effect on the maximum torque value of the PVC/E composite, compared with the value for unfilled poly(vinyl chloride), to become negligible. In the case of the composite containing only lignin in quantities of 7.5 and 10 wt % (PVC/L), reduction in the value of M_X was observed. The lignin accelerates the plasticization of the PVC blend; this effect has been previously reported [13, 15].

Moreover, it was ascertained that fusion of PVC with fillers, irrespective of their type and content in the matrix, occurs in a shorter time compared with pure PVC. The time reduction is more evident when the filler incorporates silica. The presence of such fillers in the PVC compound favors the grinding of grains into smaller morphological elements, leading to faster polymer fusion. Similar effects during the kneading of PVC blends containing $CaCO_3$ with different sizes of particles have been reported by Matuana and Kim [27] and by Tomaszewska *et al*. [26] , who assessed the fusion behaviors of rigid PVC/wood-flour composites using a torque rheometer.

Chen *et al*. [28] examined the influence of nanocarbon black (CB) on the fusion properties of rigid PVC and found that the fusion time of the PVC/CB composite decreased as the quantity of CB was increased. It was claimed that the CB particles could promote friction in the system and increase the transfer of heat and shear throughout the PVC grains.

Vicat softening temperature is very important for the utilization of the final products (see Fig. 2). An increase in this temperature by every additional degree above 90 °C in the case of PVC is a significant achievement. Softening temperature determines the possible use of many products in various types of applications. The introduction of fillers into the PVC matrix results in a systematic increase in the softening temperature, which is greater the higher the silica content of the hybrid filler. In the case of 10 wt % of a lignin/silica hybrid with a ratio of 1 : 5 wt/wt (PVC/A) the softening temperature of the composite was found to increase by 15 °C (PVC/A) compared with unfilled PVC, while the filler with equal content of the two components (PVC/C) improved the temperature by 10 °C.

Poly(vinyl chloride) (PVC) is one of the most important commercial plastic materials, but it is thermally unstable at the processing temperature. Many mechanisms of degradation of PVC have been proposed in literature, but in spite of the disagreement over the exact mechanism, it seems generally accepted that the thermal degradation of PVC proceeds with evolution of HCl *via* a chain mechanism called zipper elimination or unzipping [29].

Based on the results of the Congo red test it was found that the addition of lignin and lignin/silica fillers with a greater content of lignin (PVC/C and PVC/E) enhances the thermal stability of poly(vinyl chloride) in spite of the poor miscibility between lignin and PVC (Fig. 3). It is highly probable that the methoxy groups bonded to the phenolic rings in lignin are the methyl sources of the produced chloromethane, and this reaction consumed most of the HCl evolved from the PVC [30]. Liu Feiyue *et al.* [31] reported a very similar effect, with good improvement of the thermal stability of blends of rigid PVC with lignin treated with copolyacrylate. The authors explained this result on the basis of the sterically hindered phenol structure of lignin.

This feature of the PVC/lignin material enables safe processing without risk of thermal decomposition of the PVC. It is particularly relevant for the possibility of producing composite materials by means of conventional processing methods, for instance extrusion.

Samples of PVC composites containing 7.5 wt % of silica underwent thermal decomposition during the mea-

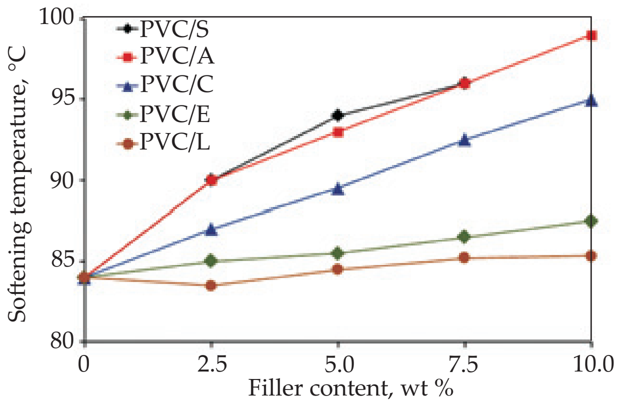

Fig. 2. Softening temperature of PVC and PVC-based composites *vs*. filler content: silica, lignin, and lignin/silica fillers in weight ratios of 1 : 5, 1 : 1 and 5 : 1 wt/wt

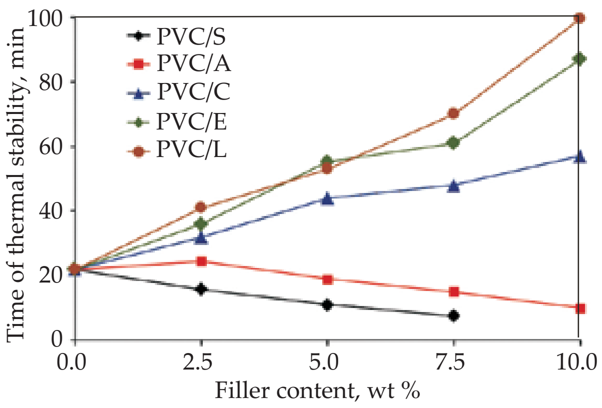

Fig. 3. Time of thermal stability of PVC and PVC-based composites *vs*. filler content: silica, lignin, and lignin/silica fillers in weight ratios of 1 : 5, 1 : 1 and 5 : 1 wt/wt

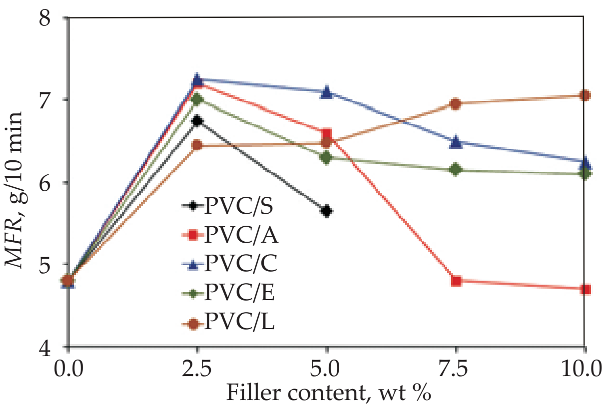

Fig. 4. ***MFR*** **of PVC and PVC-based composites *vs.* filler content: silica, lignin, and lignin/silica fillers in weight ratios of 1 : 5, 1 : 1 and 5 : 1 wt/wt**

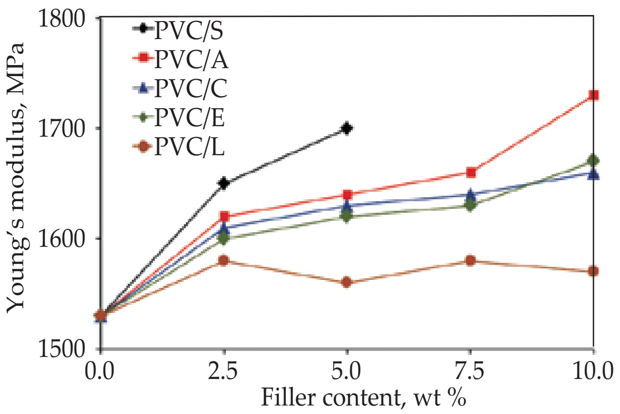

Fig. 5. Young's modulus of PVC and PVC-based composites *vs.* filler content: silica, lignin, and lignin/silica fillers in weight ratios of 1 : 5, 1 : 1 and 5 : 1 wt/wt

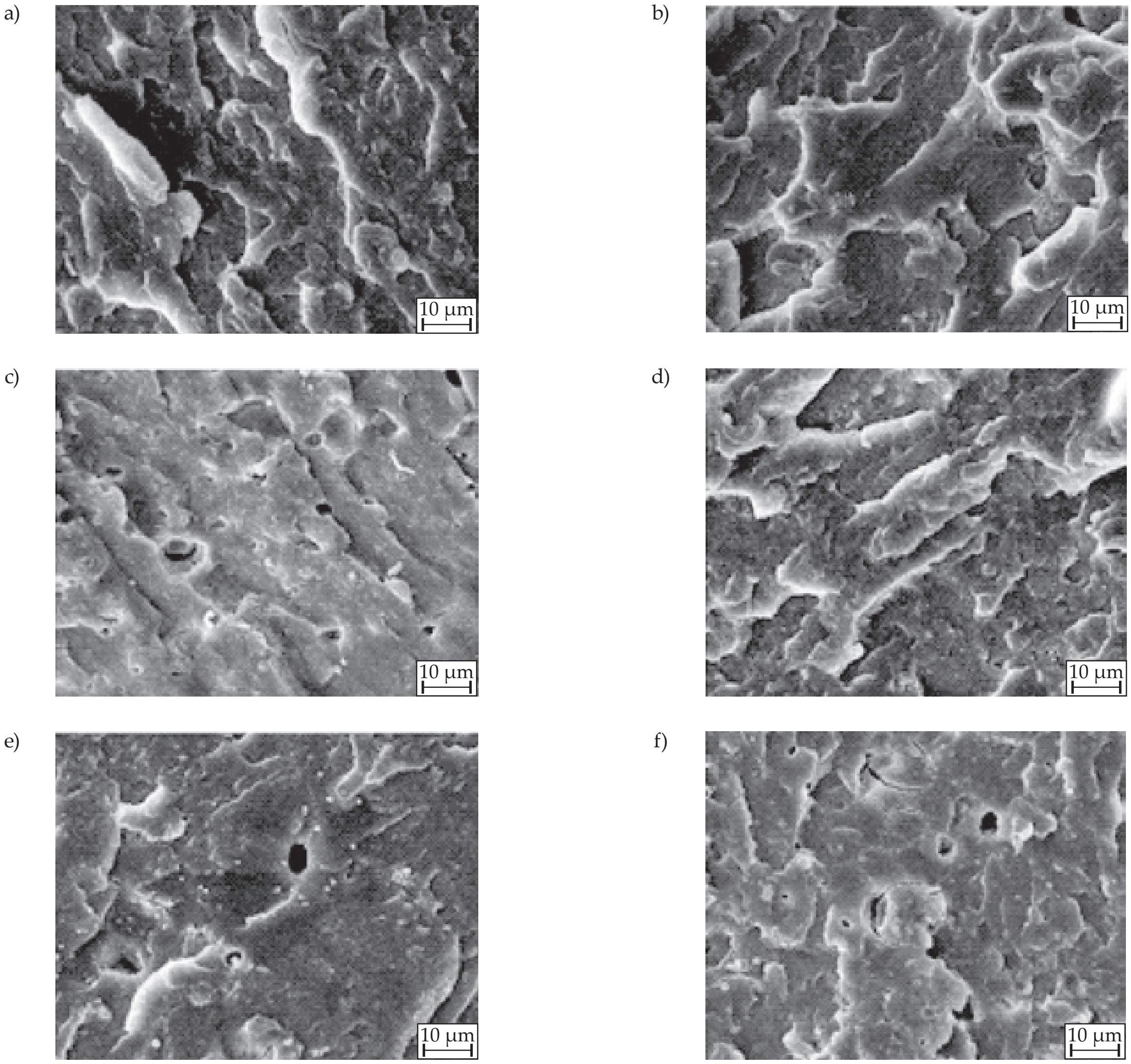

Fig. 6. SEM images of: a) pure PVC, and PVC composites with 7.5 wt % of different fillers: b) silica, c) lignin/silica hybrid (1 : 5 wt/wt), d) lignin/silica hybrid (1 : 1 wt/wt), e) lignin/silica hybrid (5 : 1 wt/wt), f) lignin

surements. Therefore, no further research was carried out on the material containing more than 5 wt % of silica. From the point of view of improvement of processing properties, the introduction of 2.5 wt % of hybrid filler into the PVC matrix seems to be the most beneficial, irrespective of its composition. The *MFR* value of such composites is higher by around 35 % (PVC/L) and by up to 50 % (PVC/C and PVC/A) compared with unfilled PVC (see Fig. 4). Further increase in the filler content in the PVC matrix causes a decrease in the *MFR* value, most rapid in the case of PVC/S and PVC/A. A different effect was observed in the case of the PVC/L composites, where increasing the content of lignin in the matrix results in a slight increase in *MFR*. This may demonstrate the plastifying properties of lignin, resulting in improvement in the processability of the PVC matrix.

The results of the investigation of tensile properties indicate that lignin/silica hybrid fillers with different proportions of components produce slight growth in the Young's modulus of composites based on a PVC matrix (Fig. 5).

The higher the concentration of hybrid filler in the matrix, and simultaneously the higher the content of silica in the hybrid filler, the greater the increase in the modulus value. Composites containing lignin have the lowest modulus of elasticity, regardless of their content in the matrix.

Based on observations made by scanning electron microscopy (Fig. 6) it may be concluded that particles of silica, lignin, and organic-inorganic hybrid fillers are distributed evenly in the PVC matrix.

The manner in which particles of the lignin/silica hybrid material are distributed is dependent on the amount of the filler incorporated in the process of production of composites. With an increase in the quantity of filler up to 10 wt %, the system displays a gradual tendency to form larger aggregate and agglomerate structures (data not shown). In summary, SEM images confirm the homogeneity of dispersion of the filler in the PVC matrix. Moreover, the surface of fractures indicates a layer structure characteristic of gelated PVC, which provides further confirmation that the conditions of processing were correctly selected.

CONCLUSIONS

It has been shown that it is possible to obtain advanced PVC-based composites containing up to 10 wt % of lignin/silica filler with various proportions of those two components, using a melt processing method.

Specific functional dual fillers have a positive influence on both the processability and functional properties of composites of unplasticized PVC, and these properties vary significantly depending on the composition of the hybrid filler. The presence of silica in a dual hybrid filler results in improvement of the functional properties of PVC composites: a higher content of silica leads to better mechanical performance and higher Vicat softening temperature. A hybrid filler with a higher content of lignin is effective in improving processing properties, especially by producing a noticeable reduction in the mechanical workload of the processing machine and increasing the thermal stability of the composites. Therefore it appears advantageous to combine these two inorganic and organic materials and to use the novel lignin/silica filler in the modification of an unplasticized PVC matrix to obtain a new material with favorable properties.

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