THE ACRYLIC/MONTMORILLONITE NANOCOMPOSITES FOR LEATHER FINISHING

ANNA BONDARYEVA¹, OLENA MOKROUSOVA^{1,2}

¹*Kyiv National University of Trade and Economics, Ukraine, Aa-aa@i.ua*

²*Kyiv National University of Technologies and Design, Ukraine, olenamokrousova@gmail.com*

Leather finishing is carried out by application of coatings that include polymer, pigment, solvents and any auxiliary products. The acrylic resins are employed in leather finishing to produce polymer film to create a uniform protective coating on the leather surface. To increase the operational properties of the polymer coating for leather finishing, it is proposed to use nanocomposites based on acrylic resin and modified dispersions of montmorillonite (AMC). The introduction of montmorillonite allows the polymer to be structured and provides improved physical and mechanical indexes of the leather coating. Acrylic polymers and colored modified dispersions of montmorillonite (CMDM) were used for the study. The colored montmorillonite was obtained by treating water dispersions of montmorillonite by sodium carbonate, basic chromium sulfate and anionic dyes. The AMC contained 1.5–2.0% montmorillonite of the dry polymer residues. The use of AMC enhances the physical and mechanical properties of the leather coating. It is shown that the use of temperature at 60 °C for the formation of finishing coating enhances the structuring of the polymer matrix, which is confirmed by the 40 % increase in the tensile strength of films and the 10 % reduction in relative elongation at break.

Keywords: montmorillonite, coating, leather finishing

INTRODUCTION

The coating, which is applied to finish the surface of the leather, contains a polymer for forming a cover film; pigment for desired color; wax emulsion for coating shine and hydrophobicity; plasticizer to reduce the stiffness of the coating film or increase frost resistance; a dispersant or emulsifier to stabilize the coating composition (Zhuravsky *et al.*, 1996; Kasyan, 2019). The largest mass fraction in the coating composition is represented by polymer (50-60 parts by weight) and pigment (10-15 parts by weight), which determines their crucial importance for the formation of a high-quality finishing coating on the leather.

The polymer is used in coating compositions as a film former to create a uniform protective coating on the leather surface. However, significant physical and mechanical loadings, multiple bending, blurring in dry and wet conditions, stretching etc. take place during leather use. This issue is especially relevant for multi-layer finishing of leather with a buffing or sanding surface. That is why the required level of the leather coating properties depends on the physico-mechanical and physico-chemical parameters of the coating films (Kasyan, 2019). Therefore, one of the ways to improve the quality of the leather coatings is the use of new effective composite materials – components of the coating compositions, which would adjust and purposefully form the necessary set of physical and mechanical properties of the polymer coating on the leather.

The use of a clay minerals has a positive structuring effect on acrylic polymers (Yilmaz *et al.*, 2011; Zhang *et al.*, 2006; Ma *et al.*, 2006).

It is known that the use of montmorillonite dispersions in sodium form helps the formation of additional chemical bonds between the surface hydroxyl groups of the mineral and the carboxyl groups of acrylate (Ma *et al.*, 2006). The established interactions provide a change in the functional properties of the polymer (Yilmaz *et al.*, 2011; Zhang *et al.*, 2006) and cause the creation of nanocomposites for the leather.

<https://doi.org/10.24264/icams-2020.I.3>

However, these composites do not paint the surface of the leather, which still requires the addition of pigment concentrate.

In order to increase the operational properties of the polymer coating for leather finishing and to make intensive-coloured surface it is proposed to use nanocomposites (AMC) based on acrylic resin and modified dispersions of montmorillonite. The use of montmorillonite makes the polymer structured and provides improved physical and mechanical indexes of the leather finishing coating.

EXPERIMENTAL

Materials

In order to get AMC nanocomposite acrylic resin (AR) and colored modified dispersions of montmorillonite (CMDM) were used for the study.

As an acrylic polymer (film former) it was used copolymer acrylic emulsion MBM – 3 (TU 6-01-196-89), which is an aqueous dispersion of a copolymer of methacrylate, butyl acrylate and methacrylic acid in the amount of 3.0 % by weight of monomers (Danylkovych *et al.*, 2009). The molecular structure of the copolymer determined sufficient elasticity and strength of the polymer in the temperature range required for coating on the leather. The emulsion was characterized by a high molecular weight, which determines the film-forming ability required for the finishing coating. The dry residue was 38.5 %, the pH – 4.35.

In order to obtain colored modified dispersions of montmorillonite, bentonite clay – $\text{Al}_2\text{O}_3 \times 4\text{SiO}_2 \times 2\text{H}_2\text{O} \times n\text{H}_2\text{O}$ (Dashukivske deposit, Cherkasy region, Ukraine) was used. The main mineral was montmorillonite, the content was 85 ± 3 %. The value of the exchange capacity was 72 mg-eq/100 g of clay. Humidity – 27 ± 3 %.

Methods

The CMDM was obtained by treating water dispersions of montmorillonite by sodium carbonate, basic chromium sulfate and anionic dyes. Namely, it was used sequential treatment of aqueous montmorillonite dispersions (100 g/l) with sodium carbonate, basic chromium sulfate and anionic dyes. The consumption of sodium carbonate was 6 % by weight of montmorillonite. Consumption of basic chromium sulfate – 10 % Cr_2O_3 by weight of the mineral, the consumption of anionic dyes in a ratio of 1:1 according to the mineral component. Colored modified dispersions of black (CMDM-B) and green (CMDM-G) montmorillonite were obtained.

AMC nanocomposites were prepared by sequentially adding to the colored modified montmorillonite, acrylic emulsion 20 % of its concentration and water to a density of 1.050–1.060 g/cm³.

Polymer films with different content of colored modified montmorillonite in the nanocomposite were formed in teflon cuvettes according to standard methods (Balberova, 1987). The polymer films were obtained by drying at 20°C, 40°C and 60°C for 48, 24 and 10 hours, respectively.

Physico-mechanical studies of polymer films based on nanocomposite AMC were performed on a rupture machine RMU-5 at a lower clamp speed of 50 mm/min according to the standard procedure (Danylkovych *et al.*, 2006). The conditional modulus of elasticity at 100 % and 300 % elongation at a temperature of 20°C, tensile strength, elongation at break were evaluated (Danylkovych *et al.*, 2006).

<https://doi.org/10.24264/icams-2020.I.3>

RESULTS AND DISCUSSION

Physico-mechanical properties of polymer films based on AMC were determined by the content of montmorillonite in the CMDM. The results of the research indicated (Fig. 1) that the conduction of CMDM dispersions into the polymer matrix AR increased the strength (σ) of the polymer films. The maximum level of strength of the films was achieved when the consumption of montmorillonite in the CMDM was more than 1.5% of the dry polymer residue (Fig. 1a, 1b). The use of montmorillonite increased in 3.5 times the modulus of elasticity (100 %) of acrylic films with an elongation of 100 % (Fig. 1, curves).

Figure 1. Physico-mechanical properties of polymer films based on AMC using CMDM-B and (a) and CMDM-G (b)

The tensile strength of films (σ_{br}) based on AMC increased to 1.81 MPa in case of using CMDM-B (Fig. 1a) and to 1.73 MPa with CMDM-G (Fig. 1b). This increase indicated that the strength of the native polymer film increased almost threefold after the using of CMDM with a consumption of 1.5-2.0 % of the dry polymer residue.

A significant increase in tensile strength (Fig. 1) of polymer films was associated with conformational strengthening of the polymer structure due to the formation of strong compact crosslinks with the involvement of active functional groups of polymer and azo dyes in colored dispersions of montmorillonite (Kovtunenکو *et al.*, 2016). Also, the use of montmorillonite nanoparticles (Mokrousova, 2010) in CMDM with a typical highly developed sorption surface of mineral particles promoted physical adsorption of the polymer and the corresponding stabilization of its structure (Kovtunenکو *et al.*, 2016; Zhang *et al.*, 2006; Ma *et al.*, 2006).

A further increase in the amount of montmorillonite above 2.5 % in case of using CMDM-G (Fig. 1b) reduced the strength of the polymer films. This effect could be observed especially when the films were stretched by 100 % and 300 %. This could be explained by the idea that the use of a significant amount of adsorption centers of montmorillonite affects the greater structuring of the polymer and leads to a decrease in its film-forming ability due to the high content of mineral particles between the polymer chains.

The presence of CMDM mineral particles in the AMC helped to adjust the relative elongation (ϵ) of polymer films (Fig. 1a, 1b, curves). The structuring of the polymer matrix with montmorillonite in the amount of 2.0-3.0 % helped to reduce the relative elongation to the level of 1100-1200 %. In the case of using CMDM-G (Fig. 1b, curve) with a montmorillonite amount of 0.25-1.5 % by weight of the polymer, there was a slight increase (3.0-3.5 %) in elasticity and the corresponding elongation of the polymer films. However, a further increase in the amount of CMDM-G to the level of 2.0 % of montmorillonite led to a decrease of 11.5 % in the relative elongation of films based on AMC (Fig. 1b, curve).

In the case of using CMDM-B (Fig. 1a, curve), a gradual decrease in relative elongation started at the montmorillonite consumption of 0.5 % from the dry polymer residue. The maximum reduction of relative elongation to the level of 1180-1200 % was typical at the montmorillonite consumption of CMDM-B more than 1.5 %.

Such changes in the physical and mechanical properties of films based on AMC were positive in the formation of a finishing coating for leather with the necessary resistance to operating loads, abrasion and repeated bending (Bondaryeva *et al.*, 2020). Excessively high level of elongation and significant viscosity of polymer films can adversely affect the quality of leather finishing due to differences in physical and mechanical loads of the polymer matrix and collagen structure (Kasyan, 2019).

Further research has shown that heat treatment of polymer films based on AMC enhanced the efficiency of their structuring and changes in physical and mechanical properties (Fig. 2).

The results of research (Fig. 2) indicated the increase in the strength of films based on AMC after thermostating at 40°C and 60°C.

Figure 2. Physico-mechanical properties of polymer films based on AMC using CMDM-B (a) and CMDM-G (b) after thermostating

The presence of CMDM-B dispersion in the composition of the AMC (Fig. 2a) increased the strength of polymer films (σ at 40°C) by 24 % after thermostating at 40°C. In the same time, applying 60°C increased the strength of films (σ at 60°C) by 40 % compared to native polymer films. For the polymer films based on AMC using CMDM-

G and consumption of montmorillonite above 1.0 % by weight of the polymer (Fig. 2b) strength values (σ at 60°C) reached the level of almost 2.0 MPa after thermostating at 60°C and there was no further change regardless of changes in mineral consumption in the AMC. The maximum effect of thermostating on the structuring of films based on AMC (Fig. 2b) was observed in the case of montmorillonite consumption in the range of 1.0 - 2.0 % of the mineral by weight of the polymer residue.

According to the results of elongation studies (ϵ) of films based on AMC (Fig. 2, curves), it was found that formation of such kind of films at 40°C and 60°C helped to reduce the tensile strength as well as the elongation of polymer films. The presence of CMDM dispersions in AMC reduced the elongation of polymer films to the level of 1000 %, which was 10 % lower compared to the same parameter at 20°C.

Our studies indicated a positive effect of thermostating at 60°C for effective structuring of AMC and improving the physical and mechanical properties of the finishing films and, subsequently, the leather coating.

CONCLUSIONS

In general, the use of mineral dispersions CMDM in the acrylic emulsion increased the physical and mechanical properties of polymer films due to their structuring, which was the result of physical adsorption and probable chemical interactions between active mineral centers and functional groups of azo dyes and polymer. The consumption of CMDM at the level of 1.5-2.0 % of montmorillonite by weight of the polymer was optimal for creating a high-quality finishing coating for leather based on AMC.

REFERENCES

- Balberova, N.A. (1987), *Directory of tanner: finishing. production control*, Moscow: Legprombytzdat, 256 p. (in Russian).
- Bondaryeva, A. and Mokrousova, O. (2020), "Formation of physico-mechanical properties of polymer-mineral coating for leather finishing", *International scientific-practical journal "Commodities and markets"*, № 2 (34), 97-107, [https://doi.org/10.31617/tr.knute.2020\(34\)08](https://doi.org/10.31617/tr.knute.2020(34)08).
- Danylkovych, A.G. (2006), *Workshop on chemistry and technology of leather and fur*. 2nd ed., Kyiv: Phoenix, 340 p. (in Ukrainian).
- Danylkovych, A.G., Mokrousova, O.R. and Okhmat, O.A. (2009), *Technology and materials of leather production*, Kyiv: Phoenix, 580 p. (in Ukrainian).
- Kasyan, E.E. (2019), *Physico-chemistry of polymer film formers for leather finishing*. Kyiv: Education of Ukraine, 178 p. (in Ukrainian).
- Kovtunencko, O., Travinskaya, T. and Mokrousova, O. (2016), "Thermal properties of anionic polyurethane composition for leather finishing", *Materials science*, 22(3), 397-402, <https://doi.org/10.5755/j01.ms.22.3.10043>.
- Ma, J., Zhang, Z., Liu, L. et al. (2006), "Application of Acrylic Coating Agent Modified by Nano SiO₂", *Journal of the Society of Leather Technologists and Chemists*, № 5, 188-193.
- Mokrousova, O.R. (2010), "Mineral fillers for leather. Rheological properties and dispersion of their aqueous suspensions", *Bulletin of KNUITD*, № 4, 256-264 (in Ukrainian).
- Yılmaz, O., Cheaburu, C.N., Gülümser, G. and Vasile, C. (2011), "Rheological behaviour of acrylate/montmorillonite nanocomposite latexes and their application in leather finishing as binders", *Progress in Organic Coatings*, 70(1), 52-58, <https://doi.org/10.1016/j.porgcoat.2010.10.001>.
- Zhang, X., Liu, Q. and Zhang, W. (2006), "Nanocomposites of Acrylate-Organosilicon Resin/Layered Silicate for Leather Finishing", *Journal of the Society of Leather Technologists and Chemists*, № 6, 250-254.
- Zhuravsky, V.A., Kasyan, E.E. and Danylkovych, A.G. (1996), *Technology of leather and fur*, Kyiv: KDUTD, 744 p. (in Ukrainian).