The mechanical and optical properties of the PVB nanocomposites with modified nanofiller

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Abstract: - Poly(vinyl butyral) (PVB) is an industrially important polymer used in laminated safety glass for its very high adhesion to glass and excellent optical properties. Clay nanofillers – clays have been frequently used in recent research. In the case of PVB, there is a possibility to deteriorate its good optical and adhesive properties. Therefore this study is focused on evaluation of optical properties of PVB nanocomposites. These were prepared by kneading in Brabender, matrix was plasticized PVB with modified nanoclay montmorillonite as fillers, namely Cloisite Na⁺. The nanoclay was modified by a grafting method; three different types of intercalation agents were used for the modification, 3-minopropyltriethoxysilane (APS), trimethylchlorosilane (TMCS) and octyltrimethoxysilane (OTMS). The modification of nanoclay was done in the proportion of nanoclay to silanes - 1:0.3. The samples were compared with pure PVB and nanocomposites with commercially modified montmorillonite, Cloisite 30B. Films of the composites were prepared by hot press molding. All nanocomposite samples had loading 0.5, 1, 2 and 3 of nanoclay. The materials were characterized by X-ray diffraction (XRD), optical microscope, tensile test and spectrophotometer. XRD determined that PVB nanocomposites reached intercalated/exfoliated structure. The Break stress of PVB nanocomposites was increased for most nanofillers. The light transmission of the PVB nanocomposites was analyzed by spectrophotometer. The data showed that the light transmission decreases with increasing loading level of nanoclay and the light transmission decreases with increasing loading level of nanoclay and the light transmission was significantly different for every nanofiller.

Key-Words: - Poly(vinyl butyral), Nanocomposite, Modified nanofillers, Grafting method, Light transmission, Tensile test

1 Introduction

PVB is sturdy and flexible. Especially, it has excellent adhesive properties with many materials such as glass, metal, plastics and wood [1]. The main use of PVB is in safety glass laminates, particularly in automotive and architectural glass. Worldwide 65 % of all PVB is used in automotive applications [2]. With increasing material costs and demands for pollution control becoming more important there is an incentive to recycle plastic waste [2-4]. An alternative to disposal in landfill is to recycle by mechanical means and basic solution central to this is an appreciation of the variation in molecular structure of PVB and its effect on mechanical properties and final use [2, 5].

In the case of PVB, there is a possibility to improve mechanical properties by mixing nanofillers with PVB. However, the optical and adhesive properties of PVB would not be to significantly change after mixing nanofillers. PVB is a polyacetal prepared by reacting polyvinyl alcohol with butyraldehyde in an acid medium [6]. Substantial amounts of unreacted vinyl alcohol units typically remain in the chain and so PVB is best regarded as a random copolymer of vinyl butyral and vinyl alcohol units [7]. The vinyl alcohol unit is polar and hydrophilic and the vinyl butyral unit is hydrophobic [7]. The hydroxyl and acetate groups act as promoters of polymer adhesives in the glass surface [8]. The decomposition mechanism of PVB is complex because PVB is a copolymer and decomposed products are very complicated [8]. The relative proportions of hydroxy groups, acetate groups and acetal groups are controlled by the conditions of the acetal reaction [8]. The final structure can be considered to be a random terpolymer of vinyl butyral, vinyl alcohol and vinyl acetate, typically 76, 22 and 2%, respectively [9]. Variations of chemical composition can occur between manufacturers and the recycled products could vary in composition and properties depending on the original source [2].

In this article, the nanoclay was modified by the grafting method; three different types of intercalation agents. From the modified nanofillers were prepared nanocomposites with PVB matrix. The morphology of nanocomposites was characterized by X - ray diffraction. In addition the optical and mechanical properties were measured.

2 Experimental

2.1 Materials

The PVB film was obtained from Retrim-CZ, under name Butacite G and it was also highly plasticized. The plasticizer amounts at 28 % of the total weight PVB. The plasticizer is under name 3GO, it is triethylene glycol di(2-ethylhexoate). PVB was used as a polymer matrix.

The following fillers were used: commercially modified montmorillonite, namely Cloisite 30B; Cloisite Na⁺. The nanoclay was modified by the grafting method in proportion nanoclay to silanes - 1:0.3; three types of intercalation agents which are summarized in Table 1.

 Table 1 – Nanofillers and modification agents

Nanofiller	Modification agent	Signification of samples
Cloisite Na ⁺	unmodified fille	Cloisite
Cloisite Na ⁺ - TMCS	trimethylchlorosilane	TMCS
Cloisite Na ⁺ - OTMS	octyltrimethoxysilane	OTMS
Cloisite Na ⁺ - APS	3-aminopropyltriethoxysilane	APS
Cloisite 30B	commercial modified filler	Cloisite 30B

2.2 Preparation of composites and specimens

The PVB composites were prepared and processed in Brabender Plasti-Corder PL 2000, equipped with a mixing chamber of 50 cm³. The mixing was performed at 160 °C using a rotational speed of 40 rpm a mixing time of 10 min and sample mass was 45 g. Thin polymer plates $(125 \times 125 \times 1 \text{ mm})$ were prepared by compression moulding after kneading in Brabender in a table press holding them at 130 °C for 5 min, sample mass was 19 g, and then cooled in a cold press. Loading level for all nanocomposite samples were 0.5, 1, 2 and 3 of nanoclay.

2.3 Instrumentations

XRD measurements were performed using PANalytical X'Pert PRO diffracto-meter with a Cu tube source ($\lambda = 0.1540$ nm) operated at 1.2 kW. The scans were taken from 2 to 7 °2Theta.

The samples for optical microscope were cut into $2 \mu m$ thick slices on a Leica RM 2255 rotary microtome. Cross sections were imaged using a Sony F717 coupled to optical microscope a Zeiss NU.

Light transmission of PVB film 1 mm thick was measured in various parts of the samples. The spectra were acquired using a spectrophotometer HE λ IOS ε in the wavelength range from 380 to 780 nm.

The tensile test was carried out at room temperature tensile testing machine Tensometr 2000. The crosshead speed was 500 mm/min and the initial gauge length was 20 mm. This method was provided under the test standard ČSN EN ISO 527-1, 3.

3 Results and discussion

Figu. 1 shows the XRD patterns of the unmodified and modified nanofillers and PVB nanocomposite (3 wt.% of nanofiller). The peaks of the nanofillers were observed around 2 and 7° 2 Theta. This indicates a change in the basal spacing of the clay in the PVB nanocomposite. It means that the structure of nanocomposites is probably well intercalated.



Fig. 1 - XRD spectra of composites with nanofillers and pure nanofillers: (I) Spectra of pure nanofillers (II) Spectra of nanocomposites (a) TMCS (b) OTMS (c) APS (d) Cloisite 30B (e) Cloisite

PVB nanocomposites tipical structure illustrated in Fig. 2 and 3. Fig. 2 shows the picture from optical microscope of PVB/Cloisite 30B nanocomposite with 2 wt.% of nanofiller. Fig. 3 shows the picture from optical microscope of PVB/TMC nanocomposite with 2 wt.% of nanofiller. Clay is dispersed in the both types of the nanocomposites as small-sized particles. The better dispersion has PVB/TMC nanocomposite, because we can see smaller particles in these nanocomposites.



Fig. 2 - Optical microscope of PVB/Cloisite 30B with 2wt.% of nanofiller.



Fig. 3 - Optical microscope of PVB/TMC with 2wt.% of nanofiller.

Fig. 4 shows the picture from optical microscope of PVB /APS nanocomposite with 1 wt.% of nanofiller. Fig. 5 shows the picture from optical microscope of PVB/APS nanocomposite with 3 wt.% of nanofiller. In the case of 1 wt.% fillers loading, the clays is better dispersed than nanocomposite with 3 wt.% of filler loading. Nanocomposite PVB/APS 3 wt.% of filler loadingAPS, it is the loading 3 wt.%, is probably too high to allow exfoliation the whole amount of the organoclay probably caused by the large aspect ratio.



Fig. 4 - Optical microscope of PVB/APS with 1wt.% of nanofiller.



Fig. 5 - Optical microscope of PVB/APS with 3wt.% of nanofiller.

Fig. 6 shows the light transmission of PVB nanocomposites with 0.5, 1, 2 and 3 loading of nanoclay. It can be concluded that the transmittances of the samples are evidently decreased with the increasing loading level of nanofiller. The best light transmission have samples PVB/Cloisite 30B and OTMS with 0.5 wt.% of nanofiller.



Fig. 6 - Light transmission of PVB nanocomposites with 0.5, 1, 2 and 3 wt.% nanofiller.

Fig. 7 shows the mechanical properties obtained from the tensile stress. The values of break stress show that the strength increased for all samples except PVB/TMC composites with 2 and 3 loading of nanoclay. The highest the break stress was achieved in the case of the PVB/Cloisite 30B with 3wt.% of nanofiller, PVB/OTMS with 0.5 wt.% of nanofiller, PVB/Cl with 2 and 3 wt.% of nanofiller. It is clear that this property is greatly influenced by the structure of the nanofiller.



Fig. 7 - Mechanical properties of PVB nanocomposites with 0.5, 1, 2 and 3 loading of nanoclay.

4 Conclusion

The influence of filler modification on the mechanical and optical properties of PVB was investigated. By the mixing nanofiller with PVB matrix, we obtained quite good dispersion. As the XRD spectrum shows, PVB composites have perhaps intercalated/exfoliated structure. According to optical microscope the nanoclays are dispersed in PVB nanocomposites as small sized particles. The Break stress of PVB nanocomposites increased for most nanofillers. However, was the transmittances of the samples are drastically decreased with increasing loading level. Future work should be focused on the improving dispersion nanofiller in PVB matrix and testing other nanofillers. There is considered that better dispersion nanofiller could be improved the optical properties of PVB nanocomposite.

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