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Possibilities of polyamide 12 with poly(vinyl chloride) blends recycling

Summary — Blends of poly(vinyl chloride) (PVC) and polyamide 12 (PA 12) were prepared by melt mixing technique in Brabender Plastograph. The samples have been studied by scanning electron microscopy (SEM), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and Charpy impact strength was tested. PVC/PA 12 blends were compatibilized with chlorinated polyethylene (CPE) and investigeted using the same methods. It was shown that such compatibilization is one of the possibilities how to get desired properties starting from brittle and immiscible PVC/PA 12 blends.
Key words — poly(vinyl chloride), polyamide, compatibilization, blend.

MOŻLIWOŚCI RECYKLINGU MIESZANEK POLI(CHLOREK WINYLU)/POLIAMID 12
Streszczenie — Za pomocą plastografu Brabendera przygotowano mieszanki poli(chlorku winylu) (PVC) i poliamidu 12 (PA 12). Otrzymane próbki badano metodami skaningowej mikroskopii elektronowej (SEM) (rys. 2), dynamicznej analizy mechanicznej (DMA) (rys. 3, tabela 1), skaningowej kalorymetrii różnicowej (DSC) (tabela 1) oraz wyznaczono udarność metodą Charpy'ego (rys. 1). Za pomocą tych samych metod zbadano zdolność mieszanek PVC/PA 12 do kompatybilizacji za pomocą chlorowanego polietylenu (CPE) (rys. 4—17). Otrzymane wyniki potwierdziły możliwości uzyskania z kruchych i niemieszalnych układów PVC/PA 12 mieszanek o pożądanych właściwościach.
Słowa kluczowe: poli(chlorek winylu), poliamid, kompatybilizacja, mieszanina.

Most polymers are thermodynamically immiscible. This fact has a negative influence on the properties of blends, which cannot reach the desired level by simple combination of two or more incompatible polymers.

Immiscibility has been indicated by separation of individual components of the blend, by coarse phase structure and bad interphase adhesion which leads to a bad inner cohesion of the material. All above leads to impossibility of using one of the simplest method of polymer blend recycling which is melt mixing technique.

Suppression of this negative tendency can be made *via* linkages (physical or chemical) at the interphase which is called compatibilization. According to the character of mixed polymers, it can be realized by several ways. Either by addition of other polymers or copolymers which have some parts of chains the same or similar to the chains of mixed polymers, or by an addition of suitable initiator which is evoking chemical reaction between polymers, or by implementation of functional groups into the macromolecular chains of mixed polymers and their post-interactions, or by application high shear stress at melt mixing technique [1]. It is obvious that the proper choice of a suitable compatibilizer plays an important role in the improvement of material pro-

perties and for this reason, the compatibilization of immiscible blends has been the subject of a broad research activity. Poly(vinyl chloride) (PVC) and polyamides (PA) can serve as examples of such immisible polymers forming heterogenous polymeric blends.

PVC/PA blends containing predominantly PA with lower melting temperature have been studied recently [2—7]. The reason is commonly known — low thermal stability of PVC.

In our previous work, we were investigated the morphology and physical properties of PVC/PA 11 blends [8]. Other type of PA with lower melting temperature is PA 12. This type of PA mixed with PVC is what we have focused in this work.

EXPERIMENTAL

Materials

The polymers and a stabilizer used were polyamide 12 (PA 12, trade name *"Rilsan"*, AESNO, ARKEMA, France), suspension poly(vinyl chloride) (PVC, trade name *"Neralit 682"*, Spolana a.s. Neratovice, Czech Republic), chlorinated polyethylene (CPE, trade name *"TYRIN 4211 P"*, Du Pont Dow Elastomers, USA, chlorine content: 42 %) and di-*n*-butyltin(bis-methylmaleate) (trade name *"Tinstab BM 400"*, Akzo Nobel, Belgium).

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Blend preparation

Binary and ternary blends (PVC/PA 12, PVC/CPE, PA 12/CPE and PVC/PA 12/CPE) were prepared in the whole concentration range. All blends contained 3 phr of thermal stabilizer *"Tinstab BM 400"*. Homogenization proceeded for 10 min in a PLE 330 Plastograph Brabender at 200 $^{\circ}$C and 50 rpm.

After blends became cold their samples were pressed at 200 $^{\circ}$C for 5+5+5 minutes (5 min preheated, 5 min pressed under pressure of 20 MPa and 5 min cooled down under the same pressure to decrease temperature up to 30—40 $^{\circ}$C).

Method of testing

Impact strength

Samples for impact strength test were prepared from pressed plates 70×60×4 mm according to ISO 179. Charpy impact strength test was made using a Resil 5,5 apparatus (CEAST, Italy) at 20 ± 1 $^{\circ}$C.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were performed using a Du Pont Thermal Analyser 990 with the view of determine of melting temperature (T_m). The samples were heated from 20 $^{\circ}$C to 220 $^{\circ}$C with a heating rate of 10 $^{\circ}$C/min. The sample mass used was about 10 mg.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) measurements leading to the glass transition temperature determination were done using a DMA DX 04T instrument (Czech Republic). Samples for DMA were cutted from pressed plates. Measurements consist of mechanical stress of the sample at defined force and measuring of deformation response at variable temperature. Rectangular specimens were strained in flexure (single cartilever). The force was constant (1000 N), frequency 1 Hz and deformation limit ±2 mm. The temperature was raised from -100 $^{\circ}$C to 100 $^{\circ}$C and scanning rate was 3 $^{\circ}$C/min.

Scanning electron microscopy

The morphology of the blends has been studied using a JEOL JSM 6100 scanning electron microscope (SEM). Surface of the sample was sputtered with gold before viewing. Some samples were extracted with selective solvents before SEM studies: xylene for CPE and tetrahydrofurane for PVC and CPE extractions.

RESULTS AND DISCUSSION

PVC/PA 12 binary blends

PVC/PA 12 blends are immiscible in the whole concentration range. This heterogeneity is expressed in a decline of mechanical properties. Dependence of impact strength values on blend composition are presented in the Figure 1. It can be seen that impact strength values of blends are lower than those of single polymers.
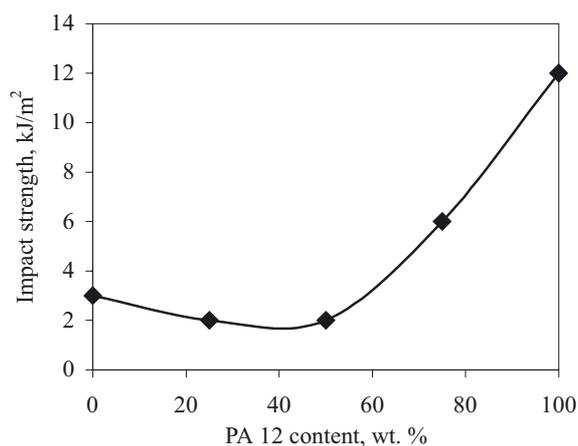

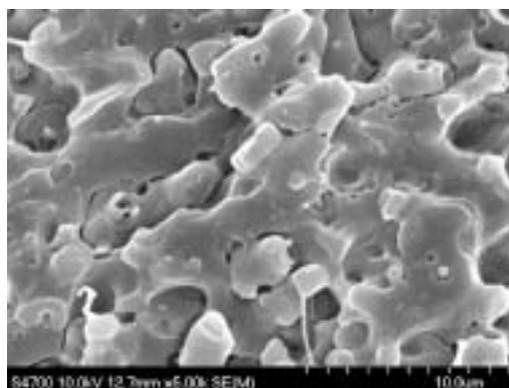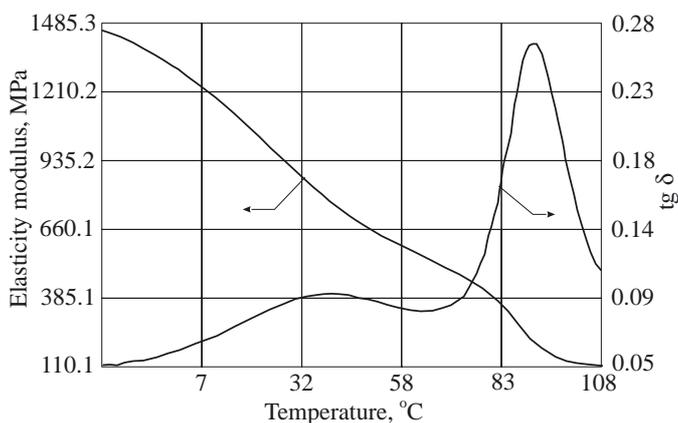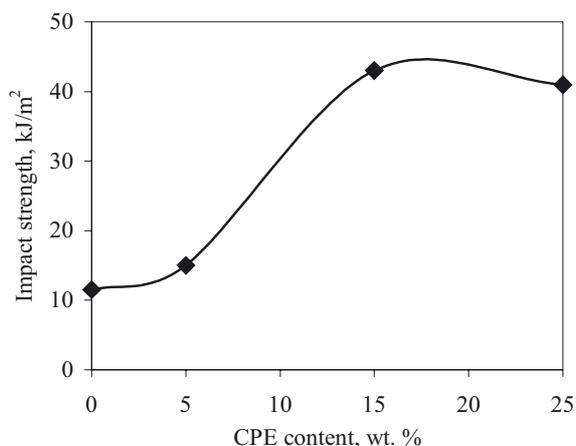*Fig. 1. Impact strength of PVC/PA 12 binary blends as a function of blend composition*

Fig. 2. SEM image of fracture area of PVC/PA 12 (50:50) blend

Fig. 3. Elasticity modulus and loss tangent (tg δ) as functions of temperature for PVC/PA 12 (50:50) blend

Also there is an evidence of heterogenity in SEM micrographs of blends fracture area. Coarse and cohesion less structure can be seen clearly in Figure 2.

T a b l e 1. Glass transition temperatures (T_g) and melting temperatures (T_m) of PVC, PA 12 and their blends

Sample composition	T_g, °C (DMA)	T_m, °C (DSC)
PA 12	40	180
PVC	85	—
PVC / PA 12 (25:75)	44; 88	181
PVC / PA 12 (50:50)	40; 90	180
PVC / PA 12 (75:25)	42; 88	179

DMA and DSC analyses showed that both amorphous and crystalline phases were not influenced with each other. So, glass transition temperatures (T_g) which can be determined by DMA analysis (the example results are presented in Figure 3) and melting temperatures (T_m) measured by DSC aproximatelly correspond to those of single polymers (Table 1).

PA 12/CPE binary blends

PA 12 mixing with CPE significantly increases impact strength of this binary system, even for small CPE doses

as it is shown in Figure 4. Huge plastic deformations and inexpressive heterogeneity can be seen in the SEM image of fracture area of PA 12/CPE (75:25) binary blends (Figure 5). However, DMA and DSC analyses confirmed that these polymers are immiscible on the molecular level. Blends show two effects corresponding to T_g, which can be observed in the Figure 6. T_m value obtained for the blend is not influenced by the presence of CPE in the sample and is equal to T_m of PA 12 (Table 2). Even though DMA measurement have indicated physical interactions between both phases T_g of CPE goes near to T_g of PA 12 (Table 2, Figure 6). Two-phase system is also clearly evident from SEM image of PA 12/CPE (75:25) blend shown in the Figure 7. There is presented a fracture area after extraction with THF there.

T a b l e 2. Glass transition temperatures (T_g) and melting temperatures (T_m) of PA 12, CPE and their blend

Sample composition	T_g, °C (DMA)	T_m, °C (DSC)
PA 12	40	180
CPE	-20	—
PA 12 / CPE (75:25)	-10; 42	180

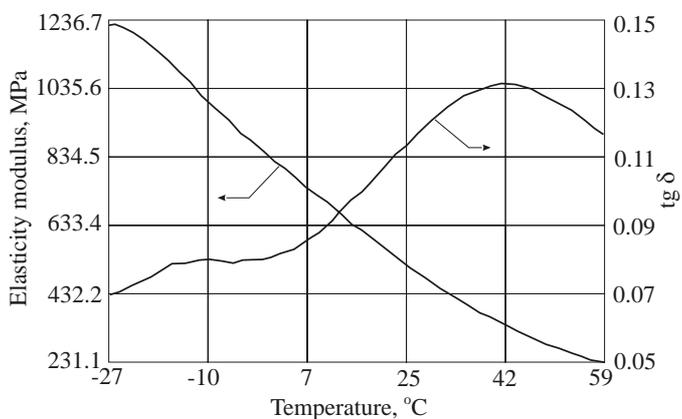Fig. 4. Impact strength of PA 12/CPE blends as a function of blend composition

Fig. 6. Elasticity modulus and loss tangent (tg δ) as functions of temperature for PA 12/CPE (75:25) blend

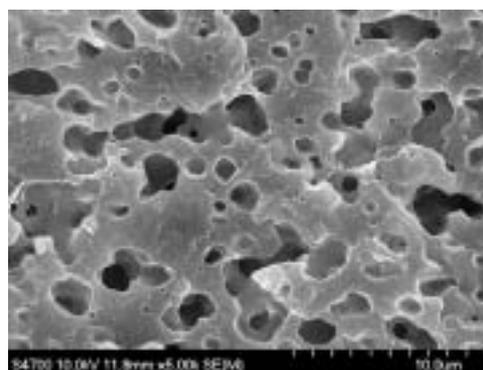Fig. 5. SEM image of fracture area of PA 12/CPE (75:25) blend

Fig. 7. SEM image of fracture area of PA 12/CPE (75:25) blend after extraction in THF

PVC/CPE binary blends

Chlorinated polyethylene is often used as a strength modifier in technological practice. It creates with PVC a microheterogeneous structure [4]. This finding corresponds to our results. As it is shown in Figure 8 impact strength increases when CPE is added to PVC. This result corresponds to the apparently quite homogeneous structure which can be seen in SEM image of PVC/CPE (75:25) blend presented the Figure 9. Actually, it is a mi-
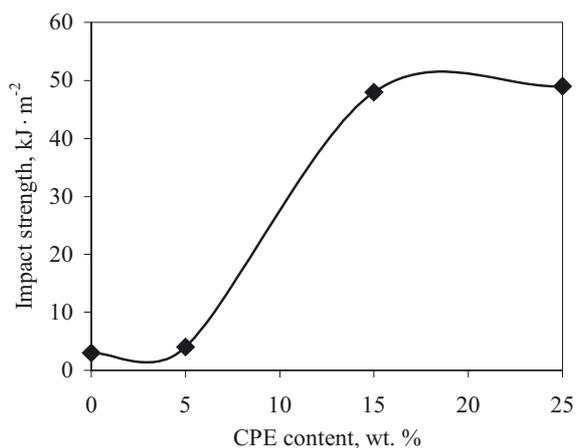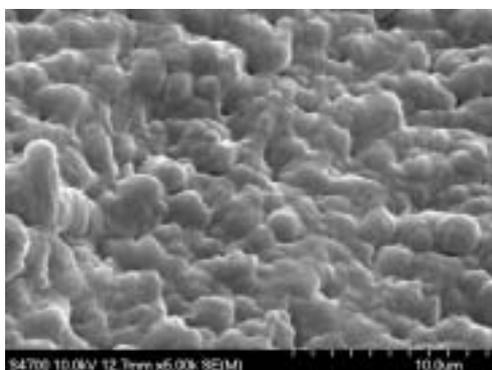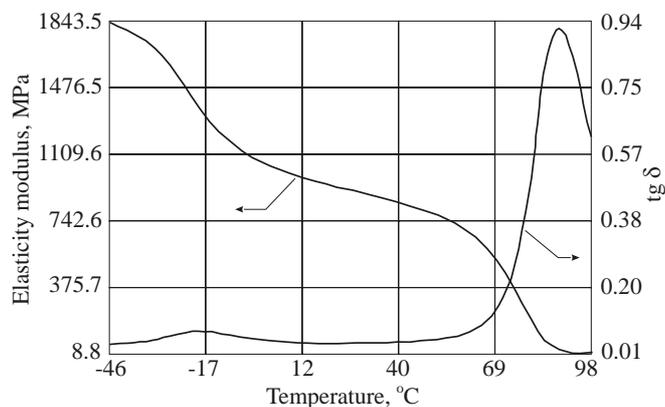

Fig. 8. Impact strength of PVC/CPE binary blends as a function of blend composition

Fig. 9. SEM image of fracture area of PVC/CPE, (75:25) blend

Fig. 10. Elasticity modulus and loss tangent (tg δ) as functions of temperature for PVC/CPE, (75:25) blend
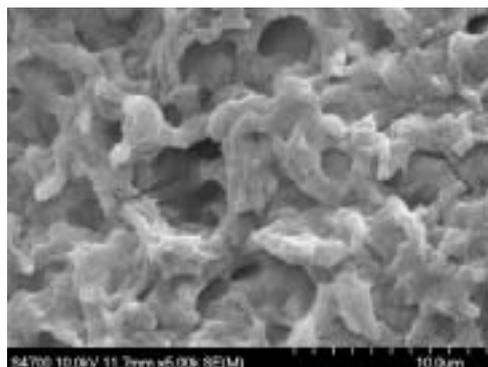

Fig. 11. SEM image of fracture area of PVC/CPE, (75:25) blend after extraction with xylene

croheterogeneous structure confirmed by presence of two glass transitions visible in Figure 10 at temperatures listed in Table 3.

T a b l e 3. Glass transition temperatures (T_g) of PVC, CPE and their blend

Sample composition	T_g, °C (DMA)
PVC	85
CPE	-20
PVC / CPE (75:25)	-20; 88

CPE can be extracted with xylene to show the heterogeneous structure of binary blend displayed in Figure 11.

PVC/PA 12/CPE ternary blends

When CPE is added to PVC/PA 12 blends, which are heterogenous and show bad mechanical properties, a material with higher impact strength than that of PVC/PA 12 binary blends is obtained (Figure 12).
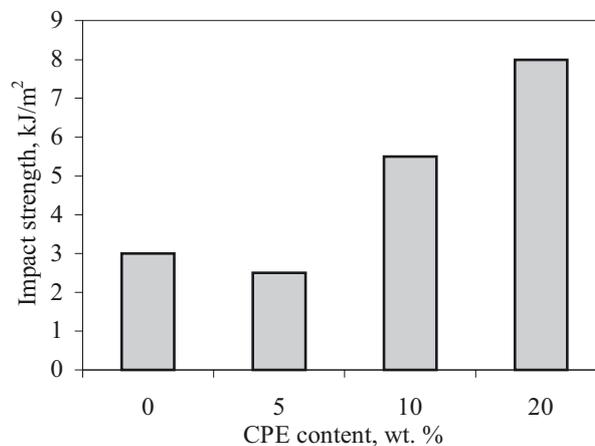

Fig. 12. Impact strength of ternary blends obtained from PVC/PA 12 (50:50) blend with addition of various amounts of CPE
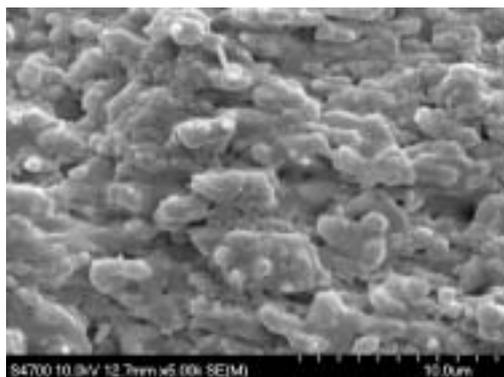
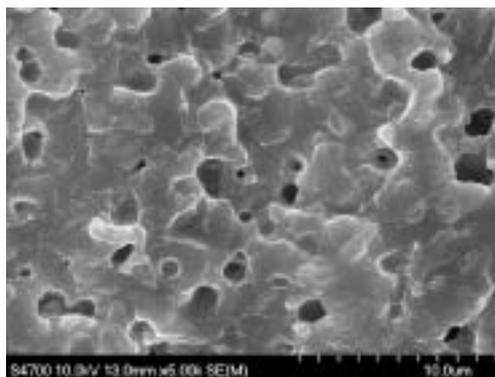Fig. 13. SEM image of fracture area of PVC/PA 12/CPE (40:40:20) blend

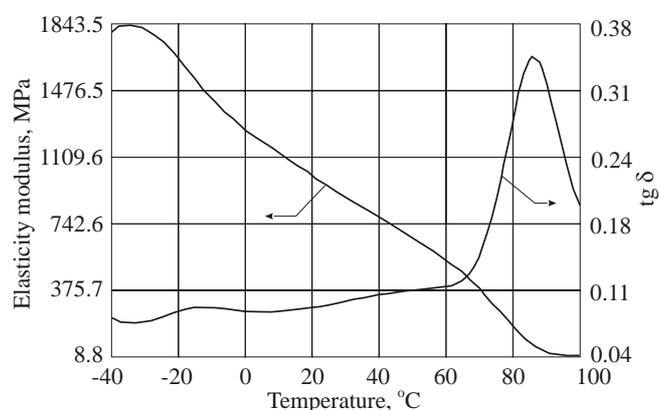Fig. 16. SEM image of fracture area of PVC/PA 12/CPE (40:40:20) blend after extraction with xylene

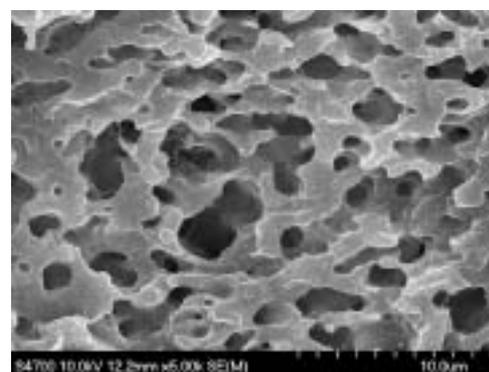Fig. 14. Elasticity modulus and loss tangent (tg δ) as functions of temperature for PVC/PA 12/CPE (40:40:20) blend

Fig. 17. SEM image of fracture area of PVC/PA 12/CPE (40:40:20) blend after extraction with THF
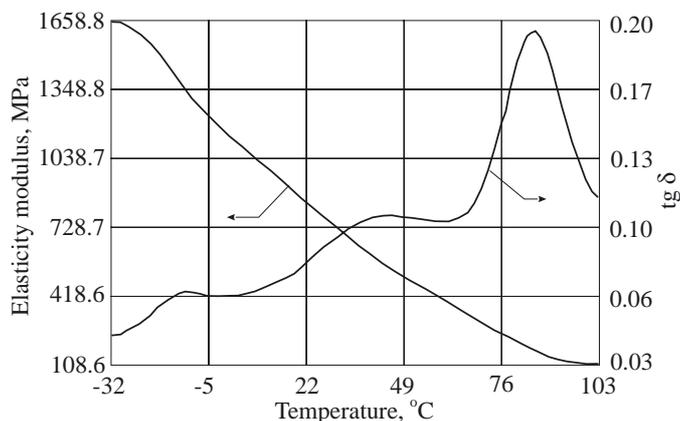
corresponding to PA 12 was indistinct. PVC or CPE can be extracted from fracture area with THF or xylene. Fracture area after xylene extraction (CPE extracted) is shown in Figure 16 and after THF extraction (CPE and also PVC extracted) in Figure 17.

CONCLUSIONS

PVC/PA 12 blends are immiscible in the whole concentration range. They have heterogeneous structure which negatively influences mechanical properties, *e.g.* impact strength. Heterogenity has been confirmed by SEM, DMA and DSC methods.

PVC/PA 12/CPE blends have higher impact strength values in comparison with PVC/PA 12 blends. SEM micrographs show that CPE positive by influence the regularity of phase dispergation. Dynamic mechanical analysis shows that PVC and PA phases are not influenced by each other. So, CPE, like a compatibilizer, represents one of the possibilities how to get desired properties of PVC/PA 12 blends, usually brittle and immiscible.

Fig. 15. Elasticity modulus and loss tangent (tg δ) as functions of temperature for PVC/PA 12/CPE (20:60:20) blend

CPE has a positive influence on the regularity of phase dispersion, which can be seen in SEM image presented in Figure 13. So, ternary blends have finer and more regular phase dispersion in comparison with that of PVC/PA 12 binary blends. Also DMA analysis shows that CPE has a significant influence on compatibilization of PVC/PA 12 blends. In the Figures 14 and 15 it can be observed that T_g corresponding to PVC decreased and T_g

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