GRAFT COPOLYMERIZATION OF ACRYLATE AND METHACRYLATE MONOMERS WITH POLY(VINYL CHLORIDE) IN EMULSION

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A direct graft copolymerization of poly (vinyl-chloride) (PVC) was carried out by using two monomers: n-butyl methacrylate and iso-butyl acrylate. Copolymerization was carried out in the emulsion with dioctyl sodium sulfosuccinate used as an emulgator, in the quantity above the critical mycelial concentration, at 80°C and with benzoyl peroxide. The graft copolymer obtained was extracted by ethyl acetate in order to remove the molecules of homopolymer which originated from the monomer used in the comopolymerization reaction and then characterized by infra red spectroscopy (FT-IR), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). FT-IR spectra of a graft copolymer prove the existence of groups of monomers used in copolymerization, which point to the achieved copolymer synthesis. The results show that the sample crystallinity decreases with the increase of the quantity of graft monomers. DSC curves show that the copolymer glass transition temperature decreases in relation to the pure poly (vinyl-chloride)- the higher content of a graft monomer leads to the larger decrease. Depending on the relative elongation, the curves of stress prove that n-butyl methacrylate and iso-butyl acrylate graft with PVC increases the value of the elongation of samples.

Introduction

Poly(vinyl chloride) (PVC) is one of the very used polymers and it is produced all over the world in enormous quantities due to its good physical properties. However, its disadvantages are poor plasticity and low thermal stability and these shortcomings are moderated by adding plasticizers, thermal stabilizers, lubricants, fillers, and other polymers. This fault of poly(vinyl chloride) can be eliminated by copolymerization with other monomers, or by subsequent graft copolymerization of the poly(vinyl chloride) [1, 2]. For graft copolymerization, PVC can be dehydrogenated, and then copolymerized by radical mechanism [3 - 6]. A number of examples of direct emulsion and suspension copolymerization of vinyl chloride and other monomers are present in the literature: ethylene [7], propylene [8], 1,3-butadiene [9], styrene [10], allyl chloride [11], vinylidene chloride [12], allyl acetate [13], vinyl acetate [14, 15], acrylonitrile [16, 17], acrylic acid [18], 2-ethylhexyl acrylate [19], methyl acrylate [20], acrylamide [21], methacrylic acid and methyl methacrylate [22], glycidyl methacrylate [23], maleic
anhydride [24], N-vinyl pyrolidone [25] etc. The purpose of this paper is to carry out
the graft polymerization of acrylate and methacrylate monomers with poly(vinyl
chloride) without dehydrochlorination.

**Experimental**

**Materials**
Poly(vinyl chloride) (Sigma-Aldrich, Wisconsin)
iso-Butyl acrylate (Sigma-Aldrich, Wisconsin)
n-Butyl methacrylate (Sigma-Aldrich, Wisconsin)
Dioctyl sodium sulfosuccinate (Sigma-Aldrich, Wisconsin)
Benzoyl peroxide (Sigma-Aldrich, Wisconsin)

**Synthesis procedure**
The copolymerization was completed in water emulsion with the emuligator dioctyl
sodium sulfosuccinate in quantities above the critical mycelial concentration at 80°C.
Benzoyl peroxide was used as the radical formation instigator. The monomers were
applied in various ratios (20, 40 and 60%) to PVC. Synthesized graft copolymers
undergo Soxlet extraction with ethyl acetate in order to extract homopolymer, which
was dissoluble in ethyl acetate and then dried at 100°C.

**Characterization of graft copolymers**

**Infra red spectroscopy with Fourier transformation (FT-IR)**
FTIR spectra of the samples were recorded in KBr pellet (0.6 mg sample, 140 mg KBr)
in the range of wavelengths from 4000 to 400 cm⁻¹ on a Bomem Hartmann&Braun
MB-series FTIR spectrophotometer.

**Differential scanning calorimetry (DSC)**
DSC curves of the samples were recorded on a DuPont DSC differential scanning
calorimeter with the scanning rate of 10°C/min in the temperature range from 30 °C to
280°C in closed aluminum pans in nitrogen atmosphere.

**X-Ray diffraction (XRD)**
X-ray diffraction was performed on a Phillips X'Pert powder diffractometer under the
following conditions: samples were exposed to monochrome CuKα radiation
(λ=1.54178 Å) and analyzed under angle 2θ between 5 and 65° with 0.05° increments
and recording time, τ=5 sec. The voltage and the strength of the electric current were
40 kV and 20 mA, respectively.

**Mechanical properties**

Breaking strain and relative breaking elongation were measured on a home
made breaking apparatus at Čerprom, Aleksinac. The samples were 100 mm in length.
30 mm wide and 2 mm in thickness. The initial operation length of the samples was 30 mm.

**Results and discussion**

Poly(vinyl chloride) reaction with radicals $R\cdot$ is followed by making a radical center in the polymer chain capable of reacting with the monomer present in the reaction mixture. Once a monomer molecule reacts with the radical center in poly(vinyl chloride) chain, other monomer molecules continue adding thus making a side chain. To achieve the effective reaction the effective mixing is needed and dioctyl sodium sulfosuccinate supplement enables a better wetting of solid poly(vinyl chloride) with a liquid monomer. Figure 1 shows a reaction scheme of the graft copolymerization poly(vinyl chloride) and $n$-butyl methacrylate.

Graft copolymerization reaction of poly(vinyl chloride) and *iso*-butyl acrylate are shown in Figure 2.

![Reaction Scheme](image)

Figure 1. Graft copolymerization poly(vinyl chloride) and $n$-butyl methacrylate
FT-IR spectra of poly(vinyl chloride) and graft copolymer poly(vinyl chloride-g-n-butyl methacrylate) with 20% of n-butyl methacrylate and 20% of iso-butyl acrylate are shown in Figures 3 and 4, respectively. FT-IR spectra of graft copolymer show a strong band at about 1730 cm\(^{-1}\) originating from C=O valence vibrations from monomers used for grafting copolymerization, n-butyl methacrylate and iso-butyl acrylate. Poly(vinyl chloride) has no C=O group so there is no band in this frequency area. In graft spectra there are also strong bands at 1158.14 cm\(^{-1}\) (in spectrum poly(vinyl chloride-g-n-butyl methacrylate) (Figure 3) and at 1168.12 cm\(^{-1}\) (in spectrum poly(vinyl chloride-g-iso-butyl acrylate) (Figure 4), originating from valence vibration of a C-O-C group of aliphatic esters not present in the poly(vynyl chloride) molecule structure.
Figure 3. FT-IR spectra of poly(vinyl chloride) and graft copolymer poly(vinyl chloride-\textit{g}-\textit{n}-butyl methacrylate) with 20% of \textit{n}-butyl methacrylate

Figure 4. FT-IR spectra of poly(vinyl chloride) and graft copolymer poly(vinyl chloride-\textit{g}-\textit{iso}-butyl acrylate) with 20% \textit{iso}-butyl acrylate

There is no significant difference in the recorded diffractograms of poly(vinyl chloride) and graft copolymers poly(vinyl chloride-\textit{g}-\textit{n}-butyl methacrylate) and poly(vinyl chloride-\textit{g}-\textit{iso}-butyl acrylate) (Figures 5 i 6). The poly(vinyl chloride) sample give a wide peak at $2\theta=8,2; 16,6; 18,8; 24,4; i 40,0^\circ$. Generally, the sample
crystallinity decreases with the increase of the quantity of grafted monomer. DSC curves confirm that the copolymer glass transition temperature is smaller in comparison to the pure poly(vinyl chloride) (Figures 7 and 8). Exothermic peaks on DSC curves of graft copolymers (curves 2 to 7) at about 130 to 170 °C originate, most probably, from the grafted copolymer acrylate segments crosslinking with PVC. Namely, the literature gives a description of heating poly(vinyl chloride) above 100°C which makes the polymer degrade and emit HCl [26]. HCl that catalyzes the elimination of HCl from the next monomer unit, resulting in the rapid unzipping of further acid to give polyene sequences. The polyenes undergo secondary reaction such as crosslinking [26].

Figure 5. X-ray powder diffraction patterns of poly(vinyl chloride) (1), graft copolymer poly(vinyl chloride-g-\textit{n}-butyl methacrylate) with 20\% (2), 40\% (3) and 60\% (4) \textit{n}-butyl methacrylate
Figure 6. X-ray powder diffraction patterns of poly(vinyl chloride) (1), graft copolymer poly(vinyl chloride-g-iso-butyl acrylate) with 20% (5), 40% (6) and 60% (7) iso-butyl acrylate.

Stress-strain curves (Figure 9) show that graft copolymers poly(vinyl chloride-g-n-butyl methacrylate) gave greater values for material strength and elongation values, while graft copolymers poly(vinyl chloride-g-iso-butyl acrylate) gave greater elongation values but the breaking strength was reduced. The strength of PVC was increased by n-butyl methacrylate, while copolymerization of PVC with iso-butyl acrylate gave PVC the plasticity and enabled an easier polymer breaking.
Figure 7. DSC curves of poly(vinyl chloride) (1), graft copolymer poly(vinyl chloride-g-\textit{n}-butyl methacrylate) with 20% (2), 40% (3) and 60% (4) \textit{n}-butyl methacrylate

Figure 8. DSC curves of graft copolymer poly(vinyl chloride-g-\textit{iso}-butyl acrylate) with 20% (5), 40% (6) and 60% (7) \textit{iso}-butyl acrylate
Table 1. Breaking strain and relative elongation values for poly(vinyl chloride) and graft copolymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Breaking strain, N/mm²</th>
<th>Elongation, %</th>
</tr>
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<tbody>
<tr>
<td>Poly(vinyl chloride)</td>
<td>2.18</td>
<td>150</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-\textit{n}-butyl methacrylate) 20 %</td>
<td>2.63</td>
<td>370</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-\textit{n}-butyl methacrylate) 40 %</td>
<td>3.20</td>
<td>302</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-	extit{iso}-butyl methacrylate) 60 %</td>
<td>3.14</td>
<td>273</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-	extit{iso}-butyl acrylate) 20 %</td>
<td>0.81</td>
<td>192</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-	extit{iso}-butyl acrylate) 40 %</td>
<td>0.83</td>
<td>222</td>
</tr>
<tr>
<td>Poly(vinyl chloride-g-	extit{iso}-butyl acrylate) 60 %</td>
<td>0.87</td>
<td>229</td>
</tr>
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The FTIR analysis show that co-polymerization has been achieved by grafting 
\textit{n}-butyl methacrylate and \textit{iso}-butyl acrylate monomers into the synthesized poly(vinyl
chloride). The investigation of physical properties shows that the properties of poly(vinyl chloride) and graft copolymers poly(vinyl chloride-g-\textit{n}-butyl methacrylate) and poly(vinyl chloride-g-\textit{iso}-butyl acrylate) are different. Curves of stress vs. relative elongation for poly(vinyl chloride) and graft copolymers also show that grafting of \textit{n}-butyl methacrylate and \textit{iso}-butyl acrylate monomers increases the elongation of the samples thus improving the physical properties of poly(vinyl chloride).

**Literature**


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Izvod

KALEM KOPOLIMERIZACIJA AKRILATNIH I METAKRILATNIH MONOMERA SA POLI(VINIL-HLORIDOM) U EMULZIJI

Naučni rad

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U ovom radu je izvedena direktna kalem kopolimerizacija poli(vinil-hlorida) (PVC) sa dva monomera: n-butil-metakrilatom i izo-butil-akrilatom. Kopolimerizacija je izvedena u emulziji pri čemu je kao emulgator iskorišćen dioktil sulfo sukcinat u količini iznad kritične micelarne koncentracije, na temperaturi od 80 °C uz benzoil-peroksid. Dobijeni kalem kopolimer je ekstrahovan etil-acetatom da odstrani molekule homopolimera nastalog od monomera koji je korišćen u reakciji kopolimerizacije, a zatim okarakterisan infracrvenom spektroskopijom (FT-IR), diferencijalnom skenirajućom kalorimetrijom (DSC) i difrakcijom X-zraka (XRD). FT-IR spektri kalem kopolimera pokazuju prisustvo grupa iz monomera korišćenih u kopolimerizaciji, što ukazuje na ostvarenu sintezu kopolimera. Time je iskorišćena osobina PVC-a da ima hlorov atom u svojoj strukturi koji se lako uključuje u prenos aktivnosti pri radikalnoj kopolimerizaciji. Rezultati pokazuju da opada kristaličnost uzoraka sa povećanjem količine kalemčenog monomera. DSC krive pokazuju da se snižava temperatura staklastog prelaza kopolimera u odnosu na čist poli(vinil hlorid) i to sniženje je veće ukoliko je veći sadržaj kalemčenog monomera. Krive napona u zavisnosti od relativnog izduženja pokazuju da se kalemčenjem n-butil metakrilata i iso-butil akrilata sa PVC-om povećava vrednost elongacije uzoraka.