STRUCTURE AND THERMAL PROPERTIES OF PEO/25A/LiBOB NANOCOMPOSITE POLYMER ELECTROLYTES

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INTRODUCTION

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) are one of the best studied polymer electrolyte systems. The structure of PEO supports ion transfer, which makes it advantageous for the preparation of solid polymer electrolytes. However, the ionic conductivity of PEO polymer electrolytes at room temperature is not satisfactory (σ =10^{-8} to 10^{-7} S cm^{-1}) due to their high degree of crystallinity. The addition of nanoparticles in the form of organically modified montmorillonite (OMT) is one of the methods to suppress its crystallization and thus provide a suitable environment for sufficient ion mobility at room temperature. In this work, nanocomposite polymer electrolytes based on PEO/Cloisite 25A complexed with lithium bis(oxalato)borate (LiBOB) were prepared and characterized. At the same time, the individual influence of Cloisite 25A (25A) on the properties of PEO/25A nanocomposites was investigated. Structural and thermal studies were performed to evaluate the potential of this system for application in rechargeable lithium-ion batteries.

EXPERIMENTAL PART AND RESULTS

PEO (Mv ~ 1 000 000, Sigma-Aldrich) (PEO10) and Cloisite 25A (Southern Clay Products) (25A) were used for preparation PEO10/25A nanocomposites and PEO10/25A/LiBOB nanocomposite polymer electrolytes, with the amount of 25A varying from 10 to 60 wt% based on the weight of PEO. LiBOB (Sigma Aldrich) was added in an amount to maintain the ratio of ether oxygen to the cation of LiBOB (EO:Li) at 8. Samples were prepared by melt intercalation method at 90 °C. Characterization was performed by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetry (TG).

Fourier transform infrared spectroscopy (FTIR)

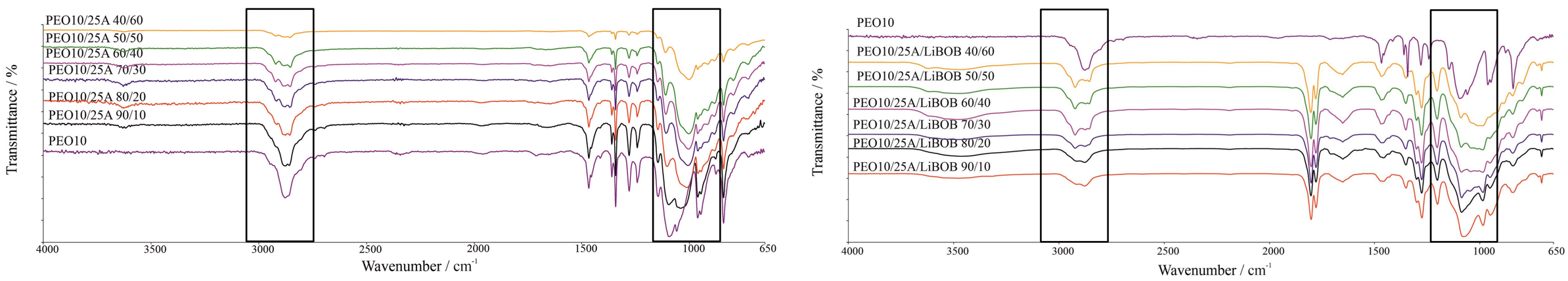

Fig. 1. FTIR spectra of PEO10, PEO10/25A nanocomposites and PEO10/25A/LiBOB nanocomposite polymer electrolytes

Differential scanning calorimetry (DSC)

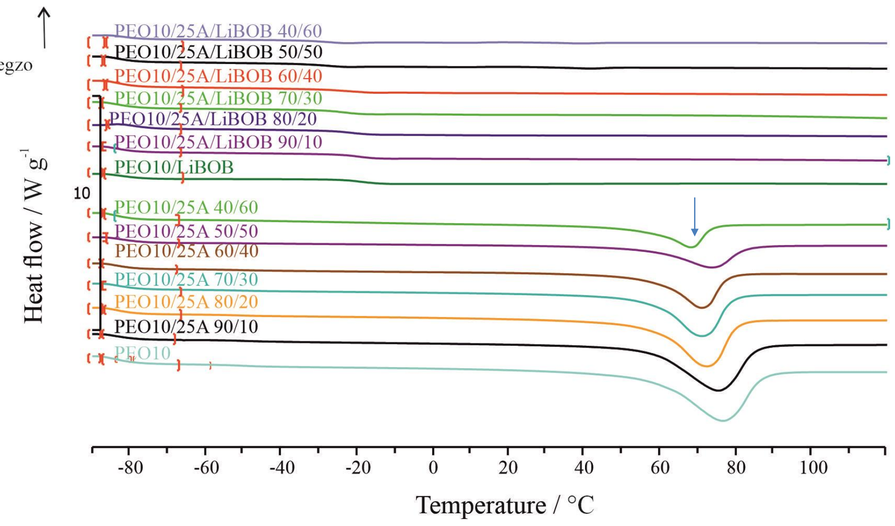

Fig. 2. DSC curves of PEO10, PEO10/25A nanocomposites, PEO10/LiBOB and PEO10/25A/LiBOB nanocomposite polymer electrolytes

Table 1. DSC characteristics of PEO10/LiBOB and PEO10/25A/LiBOB nanocomposite polymer electrolytes

		PEO10/ LiBOB	PEO10/25A/LiBOB					
DSC characteristics			90/10	80/20	70/30	60/40	50/50	40/60
T_g/°C	T_{eig}	-24	-25	-28	-27	-30	-34	-34
	T_{mg}	-19	-20	-22	-21	-22	-28	-28
	T_{efg}	-14	-15	-17	-17	-16	-23	-24
Δc_p/Jg^{-1}°C^{-1}		0,54	0,58	0,53	0,45	0,46	0,44	0,54

Table 2. DSC characteristics of PEO10 and PEO10/25A nanocomposites

		PEO10	PEO10/25A					
DSC characteristics			90/10	80/20	70/30	60/40	50/50	40/60
T_g/°C	T_{eig}	-55	-54	-55	-56	-56	-54	-48
	T_{mg}	-50	-49	-51	-51	-51	-51	-50
	T_{efg}	-46	-45	-46	-46	-45	-45	-21
Δc_p/Jg^{-1}°C^{-1}		0,19	0,15	0,13	0,11	0,12	0,05	0,25
T_m/°C	T_{eim}	57	57	58	58	58	56	56
	T_{pm}	75	74	71	70	70	73	67
	T_{efm}	87	85	80	79	77	83	73
-ΔH_m/Jg^{-1}		133,10	108,8	96,02	84,18	74,92	56,4	44,67
X_c/ %		70,76	64,27	63,81	63,39	66,38	59,97	59,37
T_c/°C	T_{eic}	42	41	43	43	44	43	44
	T_{pc}	36	33	36	36	39	36	40
	T_{efc}	21	20	25	27	30	23	31
-ΔH_c/Jg^{-1}		133,88	101,04	89,69	76,11	62,60	49,50	35,36

T_{eig} - the extrapolated onset glass transition temperature, T_{mg} - the midpoint temperature, T_{efg} - the extrapolated end glass transition temperature T_{eim} - the extrapolated onset melting temperature, T_{pm} - the peak melting temperature, T_{efm} - the extrapolated end melting temperature, ΔH_m - the melting enthalpy, X_c - the crystallinity degree, T_{eic} - the extrapolated onset crystallization temperature, T_{pc} - the peak crystallization temperature, T_{efc} - the extrapolated end crystallization temperature, ΔH_c -the enthalpy of crystallization

$$X_c = \frac{\Delta H_m}{\Delta H_0 \cdot w} \times 100$$

ΔH_0 - the melting enthalpy of 100 % crystalline PEO (205 Jg^{-1})
w - weight fraction of PEO in sample

Thermogravimetry (TG)

Fig. 3. TG curves of the non-isothermal degradation of PEO10, LiBOB, and PEO10/25A/LiBOB nanocomposite polymer electrolytes

Table 3. Characteristics of non-isothermal degradation of PEO10/25A/LiBOB nanocomposites polymer electrolytes

PEO10/25A/LiBOB		10 °C min^{-1}				
		T°/ C°	T_{max}/°C	R_{max}/% min^{-1}	m_{max}/%	m_f/%
90/10	1.	264	285	6,0	84,0	14,6
	3.	385	409	12,5	41,7	
	4.	491	500	1,5	16,8	
80/20	1.	272	288	5,0	85,1	15,7
	2.	318	335	1,3	73,0	
	3.	385	410	11,9	42,0	
	4.	491	498	1,5	18,0	
70/30	1.	271	290	4,6	86,6	21,5
	2.	322	335	1,8	75,0	
	3.	388	416	9,5	45,6	
	4.	506	518	0,8	23,1	
60/40	1.	270	291	4,4	87,7	25,9
	2.	320	338	2,2	75,7	
	3.	380	412	8,3	46,6	
	4.	501	517	0,8	27,4	
50/50	1.	275	293	3,4	90,2	30,3
	2.	321	339	2,8	78,4	
	3.	374	410	7,8	48,6	
	4.	512	504	0,6	32,0	
40/60	1.	277	301	2,4	92,1	37,2
	2.	320	345	3,8	80,1	
	3.	371	402	7,6	52,5	

$T°$ - the onset degradation temperature, T_{max} - the temperature at the maximum degradation rate, m_{max} – mass at the maximum degradation rate, m_f - residual mass

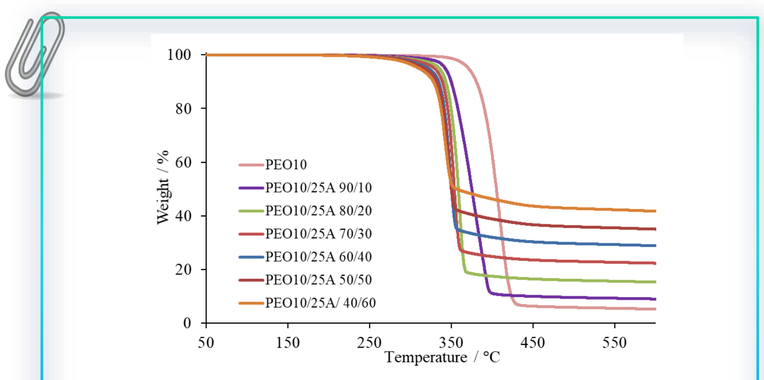

Fig 4. Characteristics of non-isothermal degradation of PEO10 and PEO10/25A nanocomposites

Table 4. Characteristics of non-isothermal degradation of PEO10 and PEO10/25A nanocomposites

PEO10/25A	10°C min^{-1}				
	T°/ °C	T_{max}/°C	R_{max}/ % min^{-1}	m_{max}/%	m_f/%
100/0	387	409	0,3	39,5	5,2
90/10	351	376	4,5	47,9	9,0
80/20	349	361	4,7	41,6	15,3
70/30	344	354	4,5	49,9	22,3
60/40	339	349	4,7	57,0	28,8
50/50	336	346	35,9	64,7	35,0
40/60	327	342	27,9	68,2	41,7

CONCLUSIONS

FTIR analysis revealed the interaction between polymer and salt. The addition of Cloisite 25A additionally affected the crystal structure of PEO in PEO10/25A/LiBOB samples. Differential scanning calorimetry (DSC) analysis showed that the addition of LiBOB in PEO10/25A/LiBOB nanocomposite polymer electrolytes causes the disappearance of the crystallinity of PEO. The increase in glass transition temperatures is caused by Li^+ coordination with PEO, which reduces the chain segmental motion of PEO. Thermogravimetric analysis (TGA) showed lower thermal stability and more complex thermal degradation process of nanocomposite polymer electrolytes compared to PEO.