THERMAL AND DIELECTRICAL STUDIES OF METHACRYLONITRILE WITH ISOBORNYL ACRYLATE AND METHACRYLATE COPOLYMERS

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ABSTRACT

Copolymers of Methacrylonitrile with Isobornyl acrylate (IBA) and Isobornyl Methacrylate (IBM) were synthesized by free radical polymerization using AIBN as initiator in dimethyl formamide (DMF) at 60±1 ^{0}C.. Thermo gravimetric analysis of the copolymers was performed and their thermal stabilities were studied. Thermal stability of IBM copolymers is found to be more than that of IBA copolymers. The dielectric properties of the copolymers were studied. The dielectric loss of the copolymers is found to be shifting to a higher temperature from acrylate to methacrylate copolymers.

Keywords:Methacrylonitrile, isobornylacrylate, isobornylmethacrylate, copolymerization,thermal and dielectric properties.*

INTRODUCTION

The copolymers of isobornylacrylate and methacrylate seem to show high tensile strength, elongation at break and upper service temperature[1]. Introduction of isobornylacrylate and methacrylate into various copolymers seem to modify and improve the properties of a number of copolymers[1,2]. In our earlier communication[3], we have discussed the copolymers of isobornyl acrylate and methacrylate with Methacrylonitrile

The present work was under taken to study the properties of copolymers of isobornylacrylate and methacrylate with Methacrylonitrile,in order to study the thermal and dielectric properties of the above synthesized copolymers.

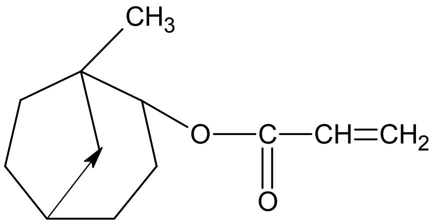
EXPERIMENTAL

Methcrylonitrile (MAN), Isobornyl acrylate (Aldrich) and Isobornyl methacrylate (Lancaster) were purified by washing with 5% solution of sodium hydroxide twice and subsequently with distilled water for three to four times. Then they are dried over calcium chloride before distilling under reduced pressure. The middle fraction of the distillate is collected and used for copolymerization.2,2$^{|}$-Azobisisobutyronitrile (AIBN) (Fluka) was crystallized from methanol. The solvent used in copolymerization was DMF which is a reagent grade chemical. This is dried and purified by distillation before use.

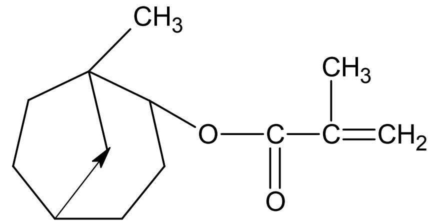
All Experiments are performed in glass tubes with appropriate quantities of dry monomers, solvents and initiator. The tubes are then sealed in an atmosphere of nitrogen and then they were introduced into the thermostat at 60 ± 1^{0}C temperature. The reaction is allowed to go for less than 10% conversion i.e., 90 min. After a given time, the polymerization mixture was poured into a large amount of water to isolate the copolymer, which was filtered and washed thoroughly with water followed by ether and hexane for purification. Then it was dried under vaccum. Different samples were prepared by changing the initial monomer feed. The initiator is used at 2.5 g/l of solvent. The total monomer concentration was maintained at 1.5 M, while the feed ratio is varied.

The monomer unit structures are represented as follows :

Methacrylonitrile, $$H_2C - \begin{array}{c} CH_3 \\ | \\ C \\ | \\ CN \end{array}$$



Isobornyl acrylate (IBA)



Isobornyl methacrylate (IBM)

RESULTS AND DISCUSSION

Thermal Studies:

Thermal stability of the copolymers MAN-IBA and MAN-IBM are determined using V5IA Dupont 2000 at a heating rate of 10^0/min. The relative thermal stabilities are evaluated by the comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) and decomposition temperature at 50% weight loss. In these copolymers, the factors that can influence thermal stability are (a) backbone structure (b) nature of the acrylate and methacrylate and (c) nitrile content.To obtain a comparative picture of relative thermal stability, initial decomposition temperature, integral procedural decomposition temperature and decomposition temperature for 50% weight loss are summarised in Table – 1

The thermal stabilities of MAN – IBM copolymers are found to be more than those of MAN – IBA copolymers shown in Fig. 1&2 This is evident from IDT and IPDT values of these copolymers. This may be attributed to the stability of the radicals formed by the decomposition process [4-7] It is also evident from the data that the acrylate copolymers are less stable than the corresponding methacrylate copolymers. The thermal stability increases with the increasing in the nitrile content. This is also evident from the data given in Tables-1.All these copolymers are undergoing decomposition in two steps.

Dielectrical Studies:

A capacitance bridge model GR 1620(WG) is used to measure the dielectric constant and dielectric loss of the MAN-IBA and MAN-IBM Ccopolymers.All samples are annealed prior to use for the measurement.

MAN-IBA Copolymers:.

Fig. 3 gives the typical plot of dielectric constant (ε') and dielectric loss (tanδ) against temperature for MAN-IBA_2 copolymer at a constant frequency of 1KHz. It is observed that as temperature increases from 30 to 240 °C the ε' value is found to increase from 4.01 to 4.61. But, the tanδ values are found to increase with increase in temperature upto 150 °C, and then decreased with further increase of temperature upto 240°C. These results are shown in Table-2.

Fig. 4 shows the temperature dependence of dielectric constant (ε') for MAN-IBA_2 copolymer at different frequencies. At any given temperature ε' values increases with increasing temperature at a constant frequency. For a temperature range of 30 to 240 °C ε' values vary from 2.91 to 3.13 at 20 KHz frequency, while from 2.99 to 3.20 at 10 KHz frequency. These observations are given in Table-3.

Fig. 5 gives the plot of temperature versus dielectric loss (tanδ) at different frequencies for MAN-IBA_2 copolymer. At a constant temperature with decrease in frequency the value of tanδ is increasing. As temperature increases from 30 to 240°C, the values of tanδ first increases, reaches a maximum and then decreases with further increases in temperature. The maximum tanδ value observed at 150°C for a frequency of 20 KHz is $4.5x10^{-2}$ while $5.6x10^{-2}$ at 10 KHz frequency. These observations are given in Table-4

MAN-IBM Copolymers:

Fig. 6 gives the temperature dependence of ε′ for MAN-IBM_2 copolymer at different frequencies. The results are given in Table-5. From the results it is observed that at any particular temperature as the frequency decreases the value of ε′ increases. The value of ε′ increases from 2.91 to 3.25 at a frequency of 20 KHz and from 3.11 to 3.76 at a frequency of 10 KHz as the temperature changes from 30 to 240 ^oC.

Fig. 7 gives the temperature dependence of tanδ for MAN-IBM_3 copolymer at different frequencies. The value of dielectric loss (tanδ) is increasing with decreasing frequency at any given temperature. At a frequency of 20 KHz, the tanδ values increases from 0.109 to 0.132 and then decreases to 0.124 as the temperature changes from 30 to 240^oC. The maximum value is observed at 180 ^oC. Similar results were observed at 10 KHz frequency also. The tanδ changes from 0.119 to 0.137.(Table 6)

Fig. 8 shows the variation of tanδ with temperature for different composition namely, MAN-IBM_1, MAN-IBM_2 and MAN-IBM_3 at a constant frequency of 1 KHz. With increase in the content of nitrile the $\tan\delta_{max}$ value shift towards higher temperature. Dipole segmental loss depends on the chemical constitution of polymers which influences intra and intermolecular interaction[8-13]. The greater the intra and intermolecular interactions, the less mobile are the repeating units, the higher is the temperature at which $\tan\delta_{max}$ occurs. The variations of tanδ with temperature for these copolymers are given in Table-7. It is observed that $\tan\delta_{max}$ changes with compositions. The maximum values observed are 180, 210 and 220 °C for MAN-IBM_1, MAN-IBM_2 and MAN-IBM_3 copolymers of different compositions respectively. Rigidity of the polymer chain is increasing with increase in –CH=CH_2 substituents in copolymer. Increase in the rigidity of polymer chain shifts $\tan\delta_{max}$ temperature towards higher ones

CONCLUSIONS

The copolymer of MAN with IBA and IBM haves been synthesized using thermal initiator in DMF. Thermal properties like T_g, IDT and IPDT have been evaluated to find the stability of the copolymers. The thermal stability of IBM copolymer is more than that of IBA copolymers.The dielectric constant and dielectric loss of the copolymer were determined to find out molecular relaxations.

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Table – 1: Thermal behaviour of methacrylonitrile with IBA and IBM copolymers

Copolymer	IDT (^oC)	IPDT (^oC)	Temperature (^oC) at wt. loss		
			10%	**20%**	**50%**
MAN-IBA_1	151.62	270.42	190.26	265.14	384.52
MAN-IBA_2	159.72	296.67	220.14	279.12	392.46
MAN-IBA_3	171.62	320.37	248.24	310.69	401.13
MAN-IBA_4	180.26	325.17	252.67	317.12	420.70
MAN-IBA_5	205.42	369.23	258.47	350.72	450.60
MAN-IBM_1	191.56	315.82	241.12	270.12	410.12
MAN-IBM_2	209.67	316.50	281.42	284.26	450.62
MAN-IBM_3	212.34	332.82	291.62	316.13	412.54
MAN-IBM_4	255.61	349.86	295.82	320.33	498.32
MAN-IBM_5	285.82	370.14	298.77	352.19	510.62

Table - 2 : Variation of ε' and tanδ with temperature for MAN-IBA_2 copolymer at 1 KHz

Temperature (^oC)	ε'	tanδ
30	4.01	0.079
60	4.08	0.081
90	4.13	0.085
120	4.19	0.091
150	4.29	0.094
180	4.37	0.090
210	4.49	0.088
240	4.61	0.087

Table – 3: Variation of ε' with temperature at different frequencies for MAN-IBA_2 copolymer

Temperature (^oC)	ε'	
	20 KHz	**10 KHz**
30	2.91	2.99
60	2.94	3.00
90	2.96	3.11
120	2.98	3.14
150	3.00	3.19
180	3.03	3.23
210	3.08	3.25
240	3.13	3.30

Table – 4: Variation of tanδ with temperature at different frequencies for MAN-IBA$_2$ copolymer

Temperature (^{o}C)	tanδ	
	20 KHz	**10 KHz**
30	0.039	0.051
60	0.041	0.053
90	0.044	0.055
120	0.047	0.058
150	0.045	0.056
180	0.043	0.054
210	0.041	0.051
240	0.039	0.049

Table – 5: Variation of ε' with temperature at different frequencies for MAN-IBM$_2$ copolymer

Temperature (^{o}C)	ε'	
	20 KHz	**10 KHz**
30	2.91	3.11
60	2.93	3.24
90	2.95	3.30
120	2.98	3.41
150	3.02	3.56
180	3.06	3.62
210	3.18	3.72
240	3.25	3.76

Table – 6: Variation of tanδ with temperature at different frequencies for MAN-IBM$_2$ copolymer

Temperature (^{o}C)	tanδ	
	20 KHz	**10 KHz**
30		
60	0.109	0.119
	0.112	0.123
90	0.117	0.125
	0.122	0.129
120	0.127	0.133
	0.132	0.142
150	0.128	0.139
180	0.124	0.137
210		
240		

Table – 7: Variation of tanδ with temperature for different compositions of MAN-IBM copolymer at 1 KHz

Temperature (^oC)	tanδ		
	MAN-IBM$_1$	MAN-IBM$_2$	MAN-IBM$_3$
40	0.110	0.168	0.151
50	0.119	0.142	0.156
60	0.124	0.146	0.161
70	0.131	0.150	0.173
80	0.138	0.156	0.179
90	0.144	0.161	0.184
100	0.151	0.168	0.188
110	0.163	0.173	0.195
120	0.174	0.179	0.210
140	0.179	0.184	0.220
160	0.181	0.189	0.232
170	0.184	0.194	0.239
180	0.199	0.211	0.242
190	0.186	0.231	0.258
200	0.182	0.250	0.264
210	0.178	0.268	0.279
220	0.172	0.249	0.284
230	0.169	0.235	0.271
240	0.167	0.231	0.69

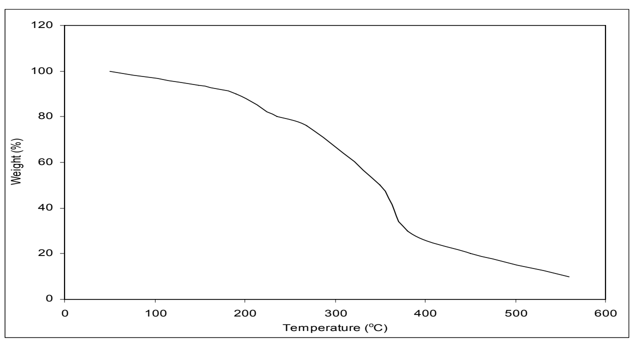

Fig. –1: Thermogram of MAN-IBA$_1$ copolymer

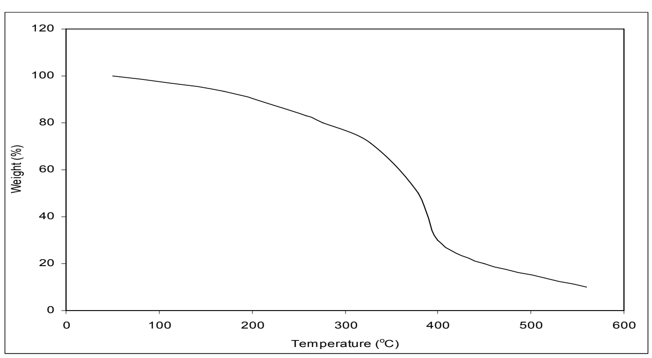

Fig.-2: Thermogram of MAN-IBM$_1$ copolymer

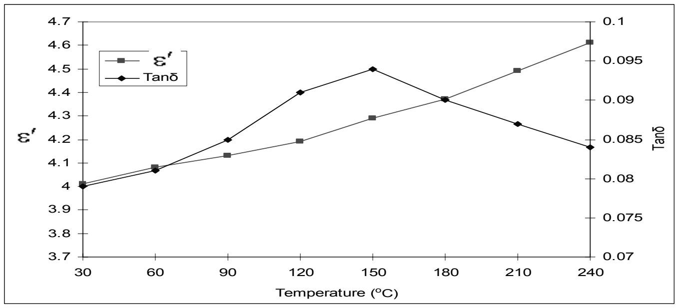

Fig.-3: Typical plot of ε′ and tanδ against temperature for MAN-IBA_2 copolymer

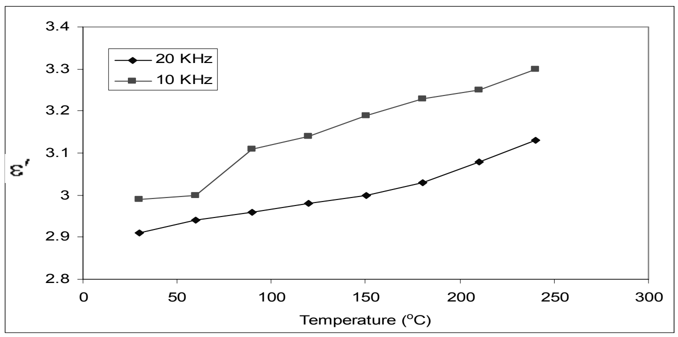

Fig.-4: Temperature dependence of ε′ for MAN-IBA_2 copolymer at different frequencies

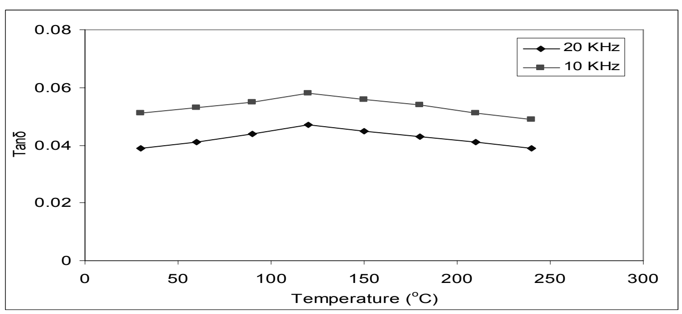

Fig. -5: Temperature dependence of tanδ for MAN-IBA_2 copolymer at different frequencies

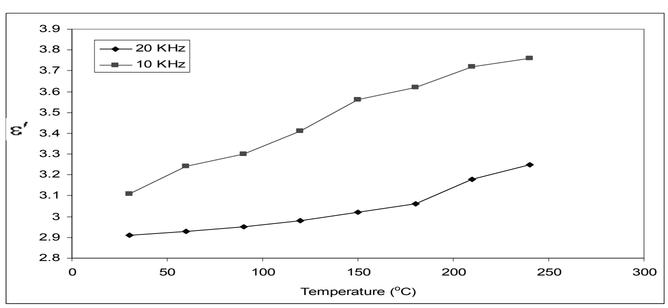

Fig.- 6: Temperature dependence of ε′ for MAN-IBM_2 copolymer at different frequencies

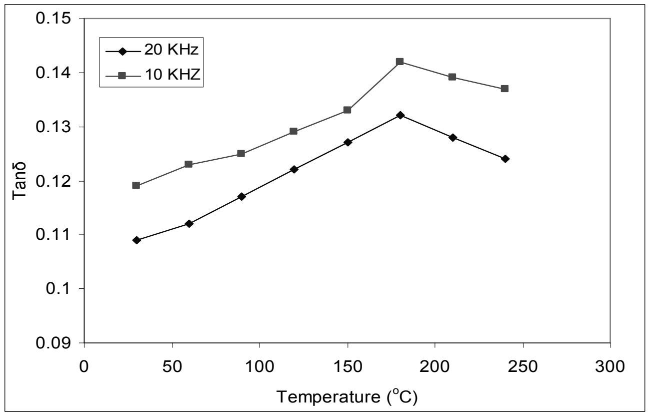

Fig.- 7 :Temperature dependence of tanδ for MAN-IBM_2 copolymer at different frequencies

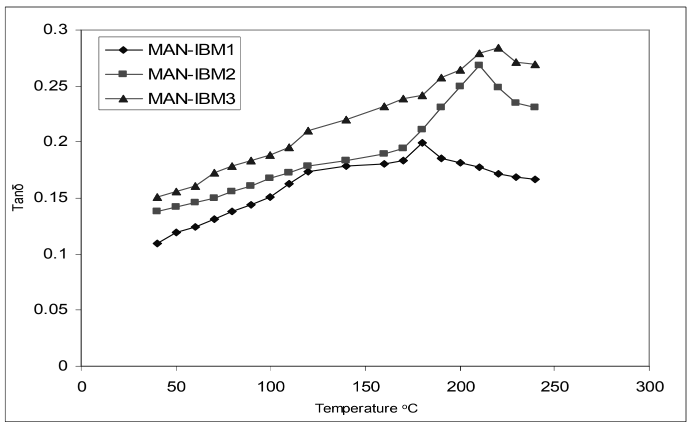

Fig.-8: Temperature dependence of tanδ for MAN-IBM copolymer at different compositions

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