TEMPERATURE DEPENDENCE OF THE THERMOPHYSICAL CHARACTERISTICS OF OLIGOMERS AND CROSS-LINKED POLYMERS BASED ON THEM

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The results of an analysis of the experimental values of the thermophysical characteristics of oligomers which are distinguished by a long and flexible oligomer block and cross-linked polymers based on them in the temperature range 90-373°K are presented.

When investigating the temperature dependence of the thermophysical characteristics of oligocarbonatemethacrylates [1] we discovered maxima in the thermal conductivity, the position and intensity of which depend on the length and flexibility of the oligomer block in these systems [2].

It is of practical importance to establish the correlation between the thermophysical characteristics of oligomer systems which have a long and flexible oligomer block and spatially cross-linked polymers based on them.

Investigations were made of oligocarbonatemethacrylates [1] with a regular position of the active and inactive groups of the bis-(methacryloxyethylenecarbonate)-ethylene glycol (OCEM), bis-(methacryl-oxyethylenecarbonate)-butylene glycol-1,4 (OCBM), bis-(methacryl-oxyethylenecarbonate)-hexamethylene glycol-1,6 (OCGM), and bis-(methacryl-oxyethylenecarbonate)-diethylene glycol (OCDM), and also cross-linked polymers based on them (PCEM, PCBM, PCGM, and PCDM), obtained by hardening oligocarbonatemethacrylates in the presence of a polymerization initiator: 0.5% cumene hydrogen peroxide and a 0.1% solution of vanadium oxide in tributylphosphate. The oligomer block of the systems investigated can be placed in the following order of degree of flexibility: OCEM < OCBM < OCGM < OCDM.

The thermophysical properties were determined in the temperature range 90-373°K by the method of adiabatic envelopes under quasistationary conditions [3]. Liquid oligomer systems were placed in a quartz cuvette in the form of a hollow cylinder with internal and external diameters of 11.5 mm and 13.0 mm, respectively, and height 100 mm. The specimens of the hardened systems have the same dimensions. A heater in the form of a cylinder was placed in thermal contact with the inner surface of the specimens. The maximum relative error in determining the thermophysical characteristics did not exceed ±5-10%.

In Fig. 1a and b we show the results of an experimental determination of the temperature dependence of the thermal conductivity and the specific heat of oligomer systems with the most rigid (OCEM) and most flexible (OCDM) oligomer blocks, and also of spatially cross-linked polymers based on them (PCEM and PCDM).

The results of an experimental determination of the thermal conductivity and the specific heat of OCM and cross-linked polymers based on them were analyzed and approximated by appropriate analytical expressions.

The initial part of the temperature dependence of the thermal conductivity $\lambda(T)$ of oligomers in the temperature range from 90°K to 170°K can be described by a hyperbolic expression of the form

$$\lambda(T) = \frac{A}{T-B} + C, \tag{1}$$

where A, B, and C are constants.

This means that the thermal conductivity of oligomers over this temperature range obeys Euken's law.

At very low temperatures (90-120°K) the temperature curve of the specific heat $C_p(T)$ of oligomer systems is given by an equation of the form

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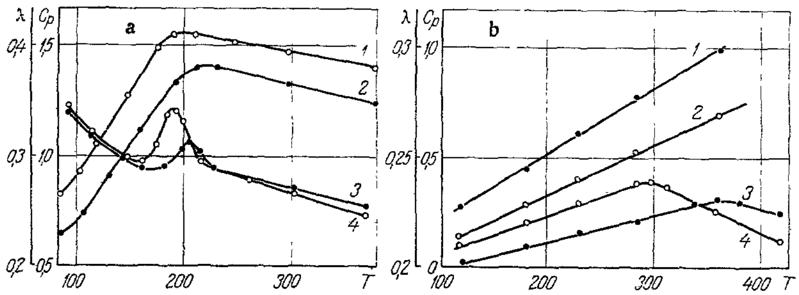

Fig. 1. Temperature dependences of the specific heat C_p (kJ/kg · deg) (1, 2) and the thermal conductivity λ (W/m · deg) (3, 4): a) oligomer systems [OCEM (2, 3) and OCDM (1, 4)] and b) polymers [PCEM (91,3) and PCDM (2, 4)]. T, °K.

$$C_p(T) = A' + B'T^3, \tag{2}$$

where A' and B' are constants.

Within the framework of Tarasov's model [4] this corresponds to the low-temperature heat capacity of three-dimensional structures.

When the temperature is raised from 220-240°K to 373°K a linear decrease in the thermal conductivity and specific heat of oligocarbonatemethacrylates occurs with a reduced value of their derivative with respect to temperature. The derivative of the specific heat with respect to temperature dC_p/dT varies from 0.08 to 0.12, while the derivative of the thermal conductivity $d\lambda/dT$ varies from 0.10 to 0.13.

We attempted to generalize the data on the thermal conductivity of oligomers in the viscous-flow state using the principle of corresponding states. As is well known, this principle was first formulated for real gases, and was then applied successfully to liquids with spherical molecules, and it was then discovered [5] that it is possible to use the method of corresponding states for liquids with chain molecules. In a further series of investigations [6, 7], the applicability of the principle to polymer liquids, particularly to solutions of thermoplastic materials, was confirmed. For strongly associated liquids, such as the oligomer systems investigated, it is possible to use the following simplified version of the method of corresponding states [8] to describe the λ(T) curves:

$$\lambda(T) = A'' + B''(1 - \tau), \tag{3}$$

where $\tau = T/T_V$, and A" and B" are constants.

Numerical values of the coefficients occurring in Eqs. (1)-(3) are shown in Table 1. Here we also give values of the derivatives of the specific heat and the thermal conductivity of these materials with respect to temperature (in relative units) in the temperature range from 220-240°K to 373°K. The oligocarbonatemethacrylates investigated are given in the table in the order in which the length and flexibility of their oligomer block increase.

When analyzing the data in Table 1 it is necessary to note the strict correlation between the coefficients of the equations describing the temperature dependences of the thermal conductivity and the specific heat of oligomer systems distinguished by the length and flexibility of the oligomer blocks, in the different temperature ranges. This correlation holds both for the linear and nonlinear parts of the λ(T) and $C_p(T)$ curves.

The nature of the oligomer has the most important effect on the absolute values of the coefficients of the temperature in Eqs. (1)-(3). These coefficients describe the rate of temperature increase (decrease) of the heat transfer when investigating the thermal conductivity and the specific heat for $C_p(T)$.

At temperatures up to T_V the coefficients A and B' increase considerably as the length and flexibility of the oligomer block increases, i.e., the greater the flexibility of the oligomer block the greater the effect a change in temperature has on the variation of the thermophysical characteristics of the oligomer in the glass-like state.

TABLE 1. Analytical Expressions Describing the Temperature Dependences of the Thermal Conductivity and Specific Heat of Oligomers

Oligomer	$T<T_V$					$T>T_V$			
	90–170K			90–120K		220–240K–373K			
	$\lambda=\frac{A}{T-B}+C$			$C_p=A'+B'T^3$		$\lambda=A''+B''(1-\tau)$		$\frac{d\lambda}{dT}$	$\frac{dC_p}{dT}$
	A	B	C	A'	$B'10^6$	A''	$B''10$		
OCEM	3,4	51,0	0,255	0,44	0,258	0,288	0,62	—0,13	—0,12
OCBM	3,45	50,5	0,260	0,47	0,265	0,290	0,58	—0,12	—0,11
OCGM	3,6	49,5	0,270	0,50	0,290	0,295	0,55	—0,11	—0,09
OCDM	3,7	49,0	0,275	0,53	0,300	0,296	0,50	—0,10	—0,08

For liquid oligomers (i.e., for $T > T_V$) the opposite phenomenon is observed: The temperature coefficients in the equations for $\lambda(T)$ and $C_p(T)$ decrease considerably as the length and flexibility of the oligomer block increases. Here an increase in the flexibility of the oligomer block leads to a reduction in the temperature dependence of the thermophysical characteristics of liquid oligomers.

The temperature dependences of the thermophysical characteristics of hardened oligomer systems polycarbonatemethacrylates (Fig. 1b) have practically linear sections with a point of discontinuity of the coefficient at the vitrification temperature of the polymer [9]. The experimental curves of $\lambda(T)$ and $C_p(T)$ of these systems are described by linear equations of general form at temperatures not exceeding the vitrification temperature of the polymer. The coefficients in these equations are shown in Table 2. Here we also give the values of the derivatives of the thermal conductivity coefficients of the polymers with respect to temperature for $T > T_V$.

It is seen from Table 2 that, as for oligomer systems, there is a correlation between the length and flexibility of the oligomer block of the initial oligomers and the coefficients in the equations describing $\lambda(T)$ and $C_p(T)$ of polycarbonatemethacrylates. Thus, when changing from PKEM to PKDM, i.e., in the direction of an increase in the flexibility of the oligomer block of the initial oligomer, the absolute values of the coefficients of the temperature in the equations describing the temperature dependence of the thermal conductivity of the polymers investigated in the glasslike state increase by a factor of practically 1.5. Similarly when $T > T_V$ the derivative of the thermal conductivity with respect to temperature increases by more than a factor 1.5 when changing from PCEM to PCDM; i.e., for the polymers investigated both in the glasslike state and in the highly elastic state there is an increase in the temperature dependence of the thermal conductivity as the length and flexibility of the oligomer block of the initial oligomer system increases. The more flexible the oligomer block the more the temperature affects the thermal conductivity of spatially cross-linked polymers based on a given oligomer.

Unlike the thermal conductivity, for the specific heat the coefficient of the temperature in the equation describing the $C_p(T)$ curve for $T < T_V$, decreases somewhat (by ≈ 20%) when changing from PCEM to PCDM. That is, the greater the length and flexibility of the oligomer block of the initial oligomer system, the less the specific heat of a polymer based on this oligomer depends on the temperature.

A comparative analysis of the data given in Tables 1 and 2 showed that for both the initial oligomer systems and for spatially cross-linked polymers based on them there is a correlation between the length and flexibility of the oligomer block and the coefficients of the temperature in the equations describing the temperature dependences of the thermal conductivity and the specific heat in different temperature ranges corresponding to different physical states of the oligomers and polymers. The glasslike state of the oligomers and polymers investigated is characterized by a similar degree of dependence of the thermal conductivity on the temperature as the length and flexibility of the oligomer block changes. The greater the length and flexibility of the oligomer block, the greater the effect the temperature has on the thermal conductivity.

The effect of the length and flexibility of the oligomer block on the specific heat of oligomer systems and cross-linked polymers based on them in the glasslike state in percentage terms is much less compared with the thermal conductivity. Also, whereas for oligomers the coefficient of the temperature increases somewhat as the length and flexibility of the oligomer block increases, for polymers based on them this coefficient falls.

These results indirectly confirm the previously obtained analogy between molecular and hypermolecular structures of oligomer systems and spatially cross-linked polymers based on them [9]. The increase in the

TABLE 2. Analytical Expressions Describing the Temperature Dependences of the Thermal Conductivity and Specific Heat of Polymers

Polymer	$T<T_V$				$T>T_V$
	$\lambda=K+LT$		$C_p=K'+L'T$		$\frac{d\lambda}{dT}$
	K	$L\cdot 10^4$	K'	$L'\cdot 10^3$	
PCEM	0,190	1,11	—0,06	3,00	—0,147
PCBM	0,190	1,28	—0,08	2,82	—0,174
PCGM	0,191	1,43	—0,11	2,51	—0,201
PCDM	0,192	1,66	—0,12	2,33	—0,231

coefficient of the temperature in the equation for λ(T) as the length and flexibility of the oligomer block increases for cross-linked polymers in the glasslike and highly states elastic, and for oligomers in the glasslike state confirms that the heat transfer in these systems is determined by the number and nature of the bonds between the structural components characterizing the density of the spatial lattice. For oligomers at temperatures above T_V the mobility of the structural components, which decrease as the dimensions of the oligomer blocks and hypermolecular structures formed from them increase, play a decisive role in the heat-transfer process. This is also confirmed by electron-microscope data. As was shown previously [9], for the OCEM oligomer with six oligomer blocks, structures of the anisodiametric play are characteristic, and for OCDM with flexible oligomer blocks hypermolecular structures of the globular type with diameters up to 1000-1500 Å are observed.

NOTATION

T	is the temperature, °K;
T_V	are the vitrification temperature, °K;
λ	is the thermal conductivity; W/m · deg;
C_p	is the specific heat; kJ/kg · deg;
A, B, C, A', B', A", B", K, L, K', L	are the constants;
$d\lambda/dT$	is the derivative of the thermal conductivity with respect to temperature;
dC_p/dT	is the derivative of the specific heat with respect to temperature, and $\tau = T/T_V$.

LITERATURE CITED

1. L. A. Sukhareva, P. I. Zubov, and G. N. Yashchenko, Inzh.-Fiz. Zh., 25, No. 2 (1973).
2. A. A. Berlin, Yu. M. Sivergin, T. Ya. Kefeli, N. L. Marshavina, N. B. Mirenskaya, and E. S. Alimpieva, VMS, 13, 2676 (1971).
3. L. L. Vasil'ev, S. A. Tanaeva, and A. D. Shnyrev, Inzh.-Fiz. Zh., 17, No. 6 (1969).
4. V. V. Tarasov, Dokl. Akad. Nauk SSSR, 100, 307 (1955).
5. J. Prigogine, The Molecular Theory of Solutions, No. 4 (1957).
6. R. Simha and A. J. Navlik, J. Am. Chem. Soc., 86, 197 (1964).
7. V. S. Nanda and R. J. Simha, J. Chem. Phys., 41, 3870 (1964).
8. T. Kh. Mukhamedzyanov and A. G. Usmanov, Thermal Conductivity of Organic Liquids [in Russian], Khimiya, Moscow (1971).
9. G. N. Yashchenko, Candidate's Dissertation, Inst. Fiz. Khim. Akad. Nauk SSSR, Moscow (1973).